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A DICTIONARY

OF

APPLIED CHEMISTRY

VOL. V.

A DICTIONARY

OF

APPLIED CHEMISTRY

BY

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ABBREVIATIONS
OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Arch. Pharm.	Archiv der Pharmazie.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Brewers J.	Brewers Journal.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Hanb.	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital.	Gazzetta chimica italiana.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie

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A
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SODIUM. Sym. Na. At.wt. 23·00.

Occurrence. Sodium is one of the commonest and most widely disseminated elements, constituting about 2½ p.c. of the solid crust of the earth. It occurs in nature in large quantities as chloride, constituting the mineral *rock-salt* or *halite*, of which very large deposits exist at Stassfurt in Germany, Northwich in Cheshire, Salzburg in Austria, and many other localities. As sodium nitrate or Chile saltpetre it forms deposits several feet thick in the rainless districts of northern Peru, and a double fluoride of aluminium and sodium (Na_3AlF_6) called *cryolite*, occurs in considerable quantity in Greenland. It is also found in nature, although in smaller quantity, as the sulphate *glauberite* $Na_2SO_4,7H_2O$; as the sesquicarbonate *trona*

$$Na_2CO_3,NaHCO_3,2H_2O,$$

and as *borax* or *tincal* $Na_2B_4O_7,10H_2O$, as a deposit in the beds of certain dried-up lakes. Many rock-forming minerals contain sodium, the most important being *albite*, soda-felspar $NaAlSi_3O_8$, *labradorite*, *oligoclase*, *sodalite*

$$Na_4(AlCl)Al_2(SiO_4)_3,$$

and *nepheline* $K_2Na_6Al_8Si_9O_{34}$, whilst it is an essential constituent of many zeolites, such as *analcime* $NaAlSi_2O_6,H_2O$, and *natrolite*

$$Na_2Al_2Si_3O_{10},2H_2O.$$

Sea water contains about 2·6 p.c. of sodium chloride, and many mineral springs and certain lakes also hold a considerable amount of this substance in solution.

Preparation of metallic sodium. A short account of the history and earlier methods for the preparation of metallic sodium has been given under POTASSIUM.

The first impulse to the preparation of sodium on a manufacturing scale was given by Deville (De l'Aluminium, Paris, 1859, 60, 120; Ann. Chim. Phys. 1856, [iii.] 46, 415; Dingl. poly. J. 134, 369; 141, 303), who employed it to replace potassium in the manufacture of aluminium. He obtained it by exposing a previously calcined mixture of sodium carbonate, coal, and chalk or lime to a white heat in wrought-iron retorts set in a furnace. Sodium distilled over, and was collected in flat receivers of peculiar shape, designed so as to offer a large condensing surface and by rapid cooling of the vapour prevent the formation of explosive compounds of the metal and carbon monoxide, although the liability to the formation of these bodies is much less than in the case of potassium. The method, however, was very costly and uneconomical, as only about one-third of the theoretical yield of sodium could be obtained.

A material improvement on this process was effected by Castner (D. R. P. 40415, 1886) in 1886, who replaced the sodium carbonate by caustic soda, and heated this with powdered carbide of iron (prepared by adding finely-divided iron to melted pitch, and coking the mixture in cylinders). This process was successfully worked on the large scale for some time and effected a considerable reduction in the price of sodium, but was eventually superseded by another process, also introduced by Castner, consisting in the electrolysis of fused caustic soda. This obviated many of the difficulties met with in the older purely chemical processes, and enabled sodium to be produced in large quantities at a relatively small cost. At the present time the whole of the sodium of commerce is manufactured electrolytically.

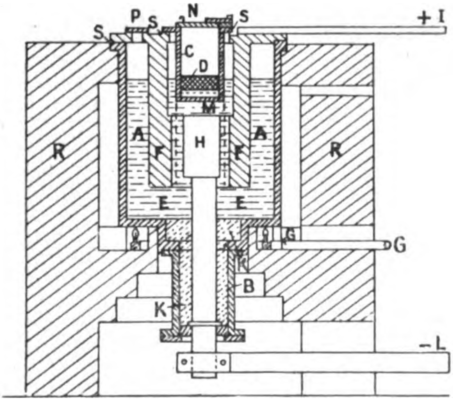

FIG. 1.

The apparatus employed by Castner (J. Soc. Chem. Ind. 1891, 777) is shown in the accompanying diagram (Fig. 1). It consists of an iron vessel A, mounted in brickwork R, in which the caustic soda is melted by means of the gas burners G. The vessel A is provided with one or more extension pipes B, through which the metallic negative electrode H passes, the intervening space K being filled with molten caustic which becomes set, and seals H in position. Immediately above this electrode is fixed a tubular iron receptacle C, fitted with a lid, N, and having a cylindrical piece of wire gauze, M, attached to its lower end. This gauze surrounds H, and rests between it and the positive electrode F. P is an opening for the escape of gas and for the insertion of a thermometer, and S is an insulating medium such as asbestos. The current is supplied through the conductors I and L. On passing the current the fused caustic soda is decomposed, and the liberated sodium D, being specifically lighter than the electrolyte, rises to the surface of the caustic in C, whence it is removed from time to time by a perforated iron spoon which allows the molten caustic to drain through while retaining the metal. Fresh caustic soda is added to the bath from time to time, thus rendering the process continuous. The size of the electrodes and their distance apart must be in proportion to the strength of the current employed. If they are too large, a quantity of the liberated sodium will dissolve in the bath and be lost through recombination, and if too small the resistance will be so increased that the bath becomes unduly heated. Any increase of temperature is followed by a proportionate loss of product and waste of energy; but it is possible so to adjust the electrical current and the quantity of alkali forming the electrolyte that the proper temperature will be maintained in a previously melted bath without applying external heat, or even by an increase of current to melt the bath, subsequently reducing the current until the proper working temperature is obtained. The apparatus is also frequently water-jacketed to assist in maintaining an even temperature. In order to secure a fair yield of the metal for the current applied it is necessary that the temperature of the electrolyte should not rise more than 20° above the melting-point of the alkali, *i.e.* should not exceed 330°. A current of 1000–1200 ampères with an E.M.F. of 4–5 volts is usually employed. Theoretically only oxygen should be liberated at the anode and sodium at the cathode; but in practice a certain quantity of hydrogen is always evolved at the cathode as well, owing to the electrolysis of the water formed in the process.

$$2OH=H_2O+O$$
$$H_2O=H_2+O.$$

Slight but harmless explosions of the hydrogen and oxygen formed sometimes take place. As one equivalent of water is produced for every two equivalents of sodium hydroxide decomposed, it is not possible to obtain more than 50 p.c. of the theoretical yield of sodium, the yield in actual working being usually nearer 40 p.c.

The Castner process is worked in England at Wallsend-on-Tyne by the Castner Kellner Co., and in Germany by the Farbwerke von Meister, Lucius & Brüning at Höchst am Main, and by the Elektrochemischen Werke Natrium at Rheinfelden. It is also operated by the Compagnie d'Electrochimie at Gavet in France, and by the Electrochemical Co. at Niagara Falls, U.S.A.

Another apparatus for the production of sodium by the electrolysis of fused caustic soda is that of Rathenau and Suter, which is used by the Electrochemischen Werke, Bitterfeld, Germany. The negative electrodes are allowed just to dip into the molten electrolyte contained in the iron vessel (Fig. 2). The surface tension causes the electrolyte to rise up slightly, so that the electrodes are not actually below the surface of the molten caustic. Metallic sodium is produced at the ends of the electrodes and partially solidifies; it is then removed by means of perforated ladles as in the Castner process. The current density in this process must not exceed 10 ampères per sq. cm.

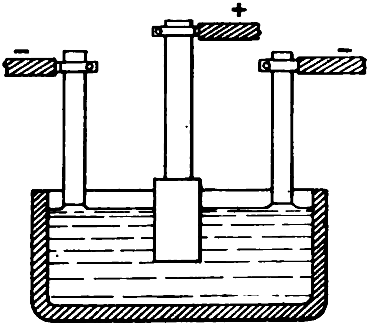

FIG. 2.

A slightly different process is that of Becker, worked by the Usines de Rioupéroux in France, a mixture of sodium carbonate and caustic soda being electrolysed in the decomposition cell shown in the following diagram (Fig. 3).

The cathode B is cone-shaped, and the sodium as it is produced rises to the collecting hood *d*, made of iron or ferronickel, and connected to the negative electrode through a resistance, so that when the metallic sodium comes into contact with the sides of the hood it is in electrical connection with the cathode, and is not further acted on by the molten electrolyte. The

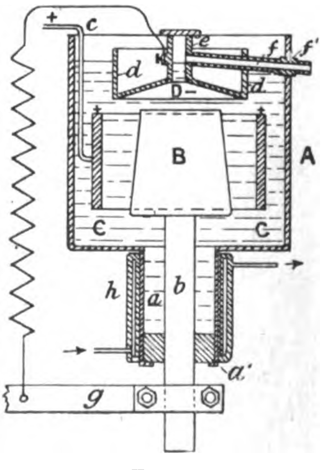

FIG. 3.

sodium being specifically lighter than the electrolyte rises in the hood and flows out through *f*. The hood *d* is cooled either by water or simply by a current of air circulating round it, so as to prevent the metal distilling over in vapour through the tube *f*, should the temperature rise too high. The temperature of the bath (550°) is much higher than in the Castner process, owing to the sodium carbonate raising the melting-point of the electrolyte. Each cell requires a current of 1250 ampères, and produces 40 kilos. of sodium in 24 hours.

The process of Darling, worked at Philadelphia, U.S.A., differs from the preceding ones in that the electrolyte consists of fused sodium nitrate. As the liberated sodium would react with the nitrate to form sodium nitrite, a divided cell is used, the anodic compartment containing fused sodium nitrate, while the electrolyte in the cathode cell consists of fused caustic soda. The Na cations are liberated at the kathode, and the NO$_3$ anions split up at the anode into NO$_2$ and O, which are passed into water to form nitric acid. The apparatus employed in the process is depicted in the accompanying diagrams (Figs. 4 and 5).

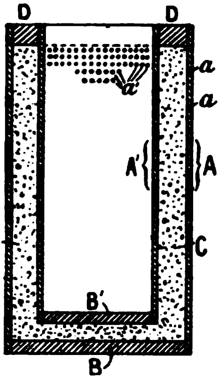

FIG. 4.

It consists of an inner cell (17) of perforated sheet iron, which is placed in an outer cell also of perforated iron, the intervening space being filled with a mixture of Portland cement and magnesia. This cell is used as the cathode compartment, and is filled with fused caustic soda. It is placed within a closed iron vessel (7), which contains molten sodium nitrate. The cathode compartment is surrounded by the iron anode formed by the cell (7), the bottom of this latter being covered to a depth of 6 ins. with Portland cement, upon which the inner cell rests. The iron outer cell (7) is connected with the positive source of current, the cathode being the 4-in. iron tube (22). About 5 p.c. of the total current is allowed to pass through the metal diaphragm (17) by means of a regulating resistance (31), and although this causes a waste of energy it greatly prolongs the life of the cell. Any gases which are generated escape by the pipe (27). At the commencement of the electrolysis the charge must be melted by applying external heat. Fresh charges of sodium nitrate are introduced into the anodic compartment from time to time, and the process thereby rendered continuous. In actual practice twelve such cells are worked together, each one taking 400 ampères at 15 volts.

Many attempts have been made to employ the cheaper sodium chloride as an electrolyte in the production of metallic sodium, but with only partial success. The chief drawback lies in the high temperature necessary to maintain the bath properly fused. At this temperature the liberated sodium unites with the excess of sodium chloride to form the so-called sodium subchloride, which either undergoes oxidation at the surface of the mass, or unites with the chlorine set free at the anode to reform the original NaCl. The intense activity of the liberated chlorine is a further objection to the process. Various attempts have been made to lower the fusing-point of the electrolyte by the addition of various salts, the most successful being that of Grabau, whose process was formerly worked commercially. It consisted of the electrolysis of a mixture of sodium chloride with either potassium chloride or alkaline earth chlorides. The addition of sodium fluoride has also been tried (Konsort. für Elektrochemie Nürnberg, D. R. P. 160540, 1904).

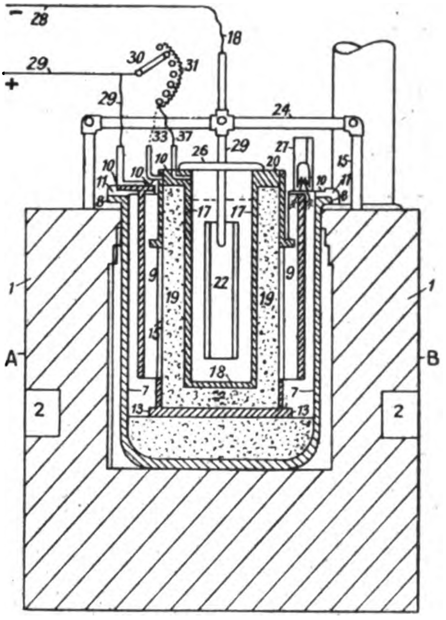

FIG. 5.

A list of patents relating to the manufacture of metallic sodium, together with an indication of the improvements claimed, is given below:—

J. Dickson, Eng. Pat. 2266, 1862 (electrolysis of the fused chloride); E. Sonstadt, Eng. Pat. 1763, 1863 (replacement of the chalk or lime in the ordinary process by gypsum); J. Anderson, Eng. Pats. 2801, 1867; 2134, 2216, 3493, 1871; 513, 1089, 1872 (heating the slag obtained by the action of hot air or steam on strongly-heated minerals containing silicates of sodium or potassium with carbon in a current of highly heated carbon monoxide); H. Larkin and W. White, Eng. Pats. 1990 and 3505, 1869; 23, 1871 (modification of the distillation process); W. Clark, Eng. Pat. 473, 1875 (electrolysis by a specially arranged current); W. Anderson Smith, Eng. Pat. 363, 1876 (use of a mixture of soda or potash with pitch, also a modified retort and condenser); W. P. Thompson, Eng. Pat. 2101, 1879 (decomposition of the hydroxide by fluid iron in a Bessemer converter); C. A. Faure, Eng. Pat. 6058, 1882, and 5489, 1883 (heating the alkaline compound in hydrogen or nitrogen by an electric current); A. L. Nolf, Eng. Pat. 4349, 1882 (electrolysis of a strong solution of sodium chloride with a mercury cathode); F. P. Harned, D. R. P. 26961, 1883 (modification of the mixture used); E. A. Höffner, D. R. P. 30377, 1884 (electrolysis of the fused chloride with a copper or silver anode); S. G. Thomas, Eng. Pat. 6367, 1884 (passage of heated water-gas through the usual mixture without applying external heat); Max Sprenger, D. R. P. 39554, 1886 (electrolysis of the chloride *in vacuô*); E. C. Kleiner-Fiertz, Eng. Pat. 8531, 1886 (electrolysis of cryolite); J. B. Thompson and W. White, Eng. Pat. 8426, 1887 (heating a coked mixture of alkaline carbonate and tar); O. M. Thowless, Eng. Pat. 12486, 1887 (use of a mixture of separately heated alkaline carbonate and coke); Curt Nelto, Eng. Pats. 14602 and 17412, 1887 (*cf.* Eng. & Min. Journal, 45, 449) (passing fused soda in a thin stream through strongly heated charcoal or coke); L. Grabau, Eng. Pat. 9904, 1887 (comprises the cooling of the cathode in electrolytic processes; the metal rises to the surface and is drawn off by a pipe); H. C. Bull, Eng. Pat. 10199, 1887 (electrolytic); A. B. Cunningham, Eng. Pat. 3601, 1888 (heating charcoal with caustic soda); G. A. Jarvis, Eng. Pat. 4842, 1888 (modification of the process for reduction by coke); W. G. Forster, Eng. Pats. 9391, 10785, and 14394, 1888 (reduction of fused alkali with coal-gas); H. M. Wallis, Eng. Pat. 12626, 1888 (modification of the mixture commonly used); W. White, Eng. Pat. 13125, 1888; H. S. Blackmore, Eng. Pat. 15156, 1888; G. M. Westman, Eng. Pat. 17736, 1888; W. White, Eng. Pat. 9784, 1889 (all relating to modifications of the mixture or distillation apparatus); T. Parker and A. E. Robinson, Eng. Pat. 11707, 1889 (electrolysis of a mixture of the hydroxide or carbonate and carbon); L. Grabau, Eng. Pat. 16060, 1890 (previously described); Castner, Eng. Pat. 13356, 1890 (previously described); H. C. Bull, Eng. Pat. 10735, 1892 (electrolysis of the fused chloride in a divided cell); C. J. T. Vautin, Eng. Pat. 10197, 1894 (production of a lead-sodium alloy by the electrolysis of fused sodium chloride with a cathode of molten lead, the alloy being run off and distilled in a retort lined with magnesia or carbon); J. A. Kendall, Eng. Pat. 23045, 1895 (reduction of a mixture of carbonate or hydroxide and carbon in hydrogen gas); G. Wolfram, Eng. Pat. 18604, 1898 (distillation of a mixture of caustic soda and calcium carbide); T. Ewan, Eng. Pat. 14739, 1902 (use of a divided cell in the electrolysis of fused caustic soda); Cassel Gold Fxtraction Co., Fr. Pat. 330987, 1903 (modified apparatus for electrolysis); T. Parker, Eng. Pat. 19196, 1903 (calcination of a mixture of sodium aluminate and carbon in an electric furnace, sodium volatilising); J. Raschen, G. Clayton, and the United Alkali Co., Eng. Pat. 2152, 1904 (employment of sodium-lead alloy as anode in electrolysis of caustic soda; P. L. Hulin, Eng. Pats. 22824, 1908; 6063, 1910 (modified apparatus for the electrolysis of fused caustic soda); A. C. Vournasos, Eng. Pat. 23689, 1908 (preparation of sodium by heating a mixture of salt and lead shot in a special furnace); Chemische Fabrik Griesheim Elektron, Eng. Pat. 29795, 1909 (heating sodium sulphide with calcium carbide); P. A. Emanuel, U.S. Pats. 957754–957756 and 957848, 1910 (production of sodium from various sodium salts by heating with carbon); R. J. McNitt, Eng. Pat. 20519, 1910 (electrolysis of fused salt in presence of lead); E. A. Ashcroft, Eng. Pats. 12377, 1903; 5013, 1910 (electrolysis of a mixture of sodamide and caustic soda with a fused lead anode); The Nitrogen Co., Eng. Pat. 20386, 1910 (formation of an alloy of sodium with a heavy metal by electrolysis, and utilisation of this as anode for electrolysing a bath of fused alkali cyanide); P. L. Hulin (J. Ind. Eng. Chem. 1911, 130) (modified apparatus for the electrolysis of caustic soda).

In the laboratory sodium can be made by a process described by Bamberger (Ber. 1898, 451), which consists in heating a mixture of sodium peroxide and charcoal or calcium carbide in a covered crucible to 300°–400°. Metallic sodium is produced, and condenses on the cover of the crucible.

$$3Na_2O_2+2C=2Na_2CO_3+Na_2.$$
$$7Na_2O_2+2CaC_2=2CaO+4Na_2CO_3+3Na_2.$$

Properties.—Freshly-cut sodium exhibits a silvery metallic lustre, which rapidly disappears on exposure to air owing to the formation of a thin film of oxide, the production of which is accompanied by a greenish phosphorescence (Linnemann, J. pr. Chem. 1858, [i.] 75, 128). According to Long (Chem. Soc. Trans. 1861, 123) sodium crystallises in acute octahedra which belong to the quadratic system.

At a temperature of −20° sodium is hard, at 0° it becomes ductile, and at the ordinary temperature it is of a waxy consistency. On heating it softens at 50° and melts at 92° (Holt and Sims, *ibid.* 1894, 65, 432), 97° (Karnakow and Puschin, Zeitsch. anorg. Chem. 1902, 30, 109). Sodium boils at 877·5° (Ruff and Johannsen, Ber. 1905, 38, 3601), giving a vapour which in thin layers appears colourless, but has a purple colour when viewed in quantity by transmitted light, and exhibits a green fluorescence. Its absorption spectrum has been examined by Roscoe and Schuster (Proc. Roy. Soc. 22, 362), and by Wood and Moore (Phil. Mag. 1903, 6, 362), and the ultra-violet portion by Wood (*ibid.* 1909, 18, 530). The sp.gr. of sodium has been determined by Baumhauer (Ber. 1873, 6, 665), who obtained the values 0·9735 at 13·5°/13·5° and 0·9943 at 10°/10°. Later determinations by Dewar (Chem. News, 1902, 85, 289) and Richards and Brink (J. Amer. Chem. Soc. 1907, 29, 117) have afforded the values 0·9724 at 0°/0° and 0·9712 at 20°/20° respectively. Ramsay (Ber. 1880, 13, 2145) found the sp.gr. of fused sodium near its boiling-point to be 0·7414. No satisfactory determination of the vapour density of sodium has at present been carried out, owing to the difficulty of finding a suitable material for the construction of the apparatus capable of resisting attack by the sodium vapour (*cf.* however Ruff and Johannsen, Ber. 1905, 38, 3602). The molecular weight of sodium was determined by Ramsay (Chem. Soc. Trans. 1889, 55, 521) by Raoult's method. He found the molecular weight to vary between 15·1 and 21·6 according to the ratio of the metal to the solvent (mercury); but the method is open to objection on account of the existence of numerous well-defined compounds of sodium and mercury.

Sodium has been obtained in the colloidal state, forming an unstable violet solution in ether, by passing an electric current of high potential by means of aluminium poles through the granular metal contained in a porcelain dish and covered with ether (Svedborg, Ber. 1905, 38, 3616).

Sodium oxidises rapidly when exposed to moist air, but can be distilled unchanged in air or even oxygen provided that all traces of moisture be excluded. It is far less readily acted on by halogens than potassium. Dry chlorine has no action on sodium, even at the melting-point of the latter (Wanklyn, Chem. News, 20, 271; Cowper, Chem. Soc. Trans. 1883, 155); neither has bromine at temperatures up to 150°, whilst sodium and iodine can be heated together to 350°–360° without combination (Merz and Holzmann, Ber. 22, 872). Dry hydrogen chloride can also be left in contact with sodium for many weeks without appreciable action resulting. The presence, however, of mere traces of water is sufficient to cause immediate and violent combination in all these cases. Heated in the air sodium takes fire and burns with a yellow flame, forming a mixture of oxides. Thrown on to cold water it swims on the surface, disengaging hydrogen and dissolving, but not evolving sufficient heat to ignite the gas. If water at 60° be used, or the free motion of the metal be hindered by increasing the viscosity of the liquid by the addition of gum or starch, the evolved hydrogen ignites, burning with a characteristic yellow flame.

With the exception of gold, silver, and copper, sodium conducts heat and electricity better than any other metal.

Metallic sodium is largely used in the manufacture of cyanides, sodamide (used in the artificial indigo industry), and sodium peroxide, and also finds application in the laboratory, being employed in many organic syntheses, in the preparation of pure caustic soda and in conjunction with alcohol as a powerful reducing agent. The most characteristic analytical reaction furnished by sodium is the intense yellow colour imparted to the non-luminous flame of a Bunsen burner by all compounds of the metal. Viewed through a spectroscope two characteristic yellow bands of wave length 5896 and 5890, known as Fraunhofer's D lines, are seen, and so delicate is this test that so small a quantity as 3×10^{-10} grm. of sodium can be detected by it. All the salts of sodium are soluble in water, so that no satisfactory precipitation reactions for its detection exist. The least soluble salts of sodium are the pyroantimoniate $Na_2H_2Sb_2O_7$, which requires 350 parts of cold water for solution, and the dihydroxytartrate. According to Ball (Chem. Soc. Trans. 1909, 2126) a solution of bismuth potassium nitrite containing cæsium nitrite forms a reagent capable of detecting as little as 0·01 mg. sodium even in the presence of considerable amount of potassium, a yellow precipitate being formed.

Sodium alloys. A large number of alloys of sodium with different metals have been prepared, the most important being those with potassium. These are liquid at the ordinary temperature and resemble mercury in appearance. They are produced either by melting the constituent metals together under rock-oil, or by fusing sodium with caustic potash (Jaubert, Ber. 1908, 41, 4116; Bull. Soc. chim. 1908, [iv.] 3, 1126). The alloy NaK_2 is now made commercially by fusing sodium with anhydrous caustic potash at a temperature of 350°. It oxidises rapidly on exposure to air, igniting spontaneously and yielding a mixture of the peroxides of sodium and potassium, which is used for the regeneration of deoxygenated air in life-saving apparatus.

Sodium and **ammonia.** Sodium dissolves in liquid ammonia with the production of an intensely blue liquid; this on evaporation yields a copper-red solid which, according to Joannis (Compt. rend. 109, 900), has the composition $NaNH_3$. The solid residue easily loses ammonia, finally leaving a crystalline mass of metallic sodium. Ruff and Geisel have, however, shown (Ber. 1906, 39, 828) that no definite chemical compound exists, and the liquid must be regarded merely as a solution of sodium in ammonia. The solution slowly decomposes on standing, with formation of sodamide—

$$Na_2+2NH_3=2NaNH_2+H_2.$$

This reaction can be considerably accelerated by the addition of platinised asbestos, which acts as a catalyst.

Sodium amalgam is best prepared by adding successive small pieces of sodium to gently warmed mercury; as each piece dissolves it produces a flash of light and emits a hissing noise. With 1 part of sodium to 100 of mercury the amalgam formed has an oily consistency, but with 80 parts of mercury to one of sodium a pasty mass results, and with smaller ratios of mercury to sodium hard crystalline amalgams are obtained. The fluid amalgams are only very slowly decomposed by water, but those containing a larger proportion of sodium react vigorously, evolving hydrogen. The rate of decomposition is greatly accelerated by the addition of a small amount of zinc sulphate or lead acetate, which acts catalytically. By allowing an amalgam containing 3 p.c. of sodium to stand under water crystals of a compound $NaHg_6$ can be obtained (Kraut and Popp, Annalen, 1871, 159, 188), which at a temperature of 40°–42° change into $NaHg_5$ (Kerp and Böttger, Zeitsch. anorg. Chem. 1900, 25, 1). Kurnakow (*ibid.* 1900, 23, 439) and Schüller (*ibid.* 1904, 40, 385) have prepared and examined a number of sodium amalgams, many of which are definite chemical compounds. According to Schüller the compound of maximum m.p. (360°) possesses the formula $NaHg_2$. If sodium amalgam be treated with solutions of the other alkalis or alkaline earths, partial replacement occurs, an amalgam of the metal employed being produced (Byers, J. Amer. Chem. Soc. 1908, 30

1584; Böttger, J. pr. Chem. 3, 283). Sodium amalgam is employed in the laboratory as a reducing agent, and an amalgam containing 2–3 p.c. of sodium is used to some extent in gold extraction processes to prevent the 'sickening' of the mercury by reducing the oxide of the base metals which collect on it and interfere with the proper working of the process.

Sodium Compounds.

Only two well-defined oxides of sodium are known, *i.e.* the monoxide Na_2O and the dioxide Na_2O_2, although according to Johannis (Ann. Chim. Phys. 1906, [viii.] 7, 75) a sesquioxide Na_2O_3 can be obtained by the action of oxygen on sodammonium.

Sodium monoxide is produced, together with the dioxide, by the combustion of sodium in air or oxygen. If the supply of oxygen be limited and the sodium be not heated above 180°, only the monoxide is formed (Holt and Sims, Chem. Soc. Trans. 1894, 442). It can be obtained perfectly pure by partially oxidising the metal and separating the unchanged sodium by distillation *in vacuô* (Rengade, Compt. rend. 1906, 143, 1152). The monoxide is also formed when metallic sodium is heated with the nitrite or nitrate, nitrogen being liberated.

Sodium monoxide is a white, hygroscopic substance of sp.gr. 2·27, and melts at a red heat. Hydrogen reduces it to metal at 170°–180° (Rengade, Ann. Chim. Phys. 1907, [viii.] 11, 424). It combines with fluorine, iodine, and sulphur with incandescence, and reacts violently with water, forming sodium hydroxide.

Sodium dioxide or **peroxide** is obtained when the metal is burned in an excess of air or oxygen. It is now made on the large scale according to Castner's process (Eng. Pat. 20003, 1891), which consists in placing sodium on aluminium trays loaded on to small waggons, which are then run through an iron tube, provided at each end with tightly-closing iron doors, set in a furnace and heated to 300°. A current of dry air, free from carbon dioxide, is passed through the tube, the peroxide produced being withdrawn at one end and fresh charges of sodium introduced at the other. The technical product thus obtained contains about 93 p.c. of sodium peroxide. Pure sodium peroxide is yellow and, unlike the monoxide, is not deliquescent (Jaubert, Compt. rend. 1901, 132, 35). It absorbs carbon dioxide with formation of sodium carbonate and liberation of oxygen, and a mixture of this oxide with potassium peroxide is used in life-saving apparatus to regenerate air contaminated by respiration. With CO it yields sodium carbonate, and with N_2O and NO sodium nitrite. Charcoal and the alkaline earth carbides reduce it to metallic sodium at a temperature of 300°–400° (Bamberger, Ber. 1898, 31, 451). Although sodium peroxide is not decomposed when heated alone it readily gives up oxygen to other substances mixed with it, and hence is largely used in the analysis of many refractory minerals, such as pyrite and chromite. As fused sodium peroxide acts most energetically on platinum, iron, &c., it is necessary to use crucibles of nickel, as this is less attacked than other metals. In the presence of moisture the peroxide acts powerfully on organic substances such as paper, oxidation frequently taking place with explosive violence. Sodium peroxide dissolves readily in water with formation of caustic soda and hydrogen peroxide, a portion of the latter simultaneously undergoing decomposition into water and oxygen owing to the heat evolved during solution. By exposing the peroxide to moist air free from carbon dioxide, or by the cautious evaporation of its solution in cold water, tabular hexagonal crystals of a hydrate $Na_2O_2,8H_2O$ can be obtained, which on standing over sulphuric acid lose water, forming the dihydrate

$$Na_2O_2,2H_2O.$$

The octahydrate is also produced by adding 1½–2 times its volume of alcohol to a solution of caustic soda and hydrogen peroxide (Schöne, Annalen, 1878, 193, 241). The hydrate dissolves in cold water without decomposition, but on heating the solution oxygen begins to be evolved at 30°–40°, the decomposition of the salt being complete at 100°.

Sodium peroxide is employed as an oxidising agent, as a source of oxygen in the laboratory, and in the preparation of bleaching solutions containing hydrogen peroxide.

Sodium hydroxide, *see Caustic Soda*, p. 45.

Sodyl hydroxide. According to J. Tafel (Ber. 1894, 27, 816, 2297), a substance of the formula $O:Na{\cdot}OH$ is produced by the action of absolute alcohol on sodium peroxide at 0°, according to the equation

$$Na_2O_2+C_2H_5OH=NaOC_2H_5+O:Na{\cdot}OH.$$

It is a white powder, soluble in cold water, the solution decomposing on heating into caustic soda and oxygen, the same decomposition taking place with explosion when the dry substance is heated.

Sodium fluoride NaF occurs native in small quantities in nepheline syenite in the Los Islands, and in considerable amount as the double fluoride of aluminium and sodium, *cryolite* ($3NaF{\cdot}AlF_3$), found in Greenland. It may be obtained from this latter source by treating the powdered mineral with an excess of strong caustic soda solution in iron pans, whereby the alumina is dissolved and sparingly soluble sodium fluoride remains behind. The pure salt is best made by neutralising a solution of hydrofluoric acid with sodium hydroxide or carbonate.

Sodium fluoride crystallises in colourless cubes of sp.gr. 2·766 (Schröder), which on heating melt at about 900°, but volatilise slightly at a lower temperature. The salt is only sparingly soluble in cold water (100 parts of water at 15° dissolve 4 parts NaF) and the solubility increases only slightly with the temperature. For the electrical conductivities of solutions of sodium fluoride of varying strengths, see Kohlrausch and Steinwehr (Sitz. der Berl. Akad. 1902, 581).

Sodium fluoride unites with hydrofluoric acid to form an acid salt, $NaF{\cdot}HF$, which can be obtained in rhombohedral crystals from a solution containing an excess of hydrofluoric acid. The crystals decompose on heating, evolving HF and leaving sodium fluoride. A number of double fluorides of sodium with other metals have also been prepared, for which see Wagner, Ber. 19, 896.

Uses. Sodium fluoride is occasionally employed as an antiseptic, and has been recommended for use in lotions in certain affections of the skin.

Sodium chloride. *Chlorure de sodium, hydrochlorate de soude, sel marin*, Fr.; *Steinsalz, Kochsalz, Salz, Salzaures Natrium, Chlornatrium*, Ger.; *sal*, Lat.; Ἅλς, Greek.

Sodium chloride, or common salt, is found in nature as the mineral *halite*, or *rock salt*. It crystallises in cubes, occasionally associated with other forms derived from the regular system. Hardness, 2; sp.gr. 2·2. It is colourless and transparent when pure, but is usually tinged yellow, red, brown, or green.

Owing to its wide distribution on the earth salt has been known from the very earliest times. It is frequently mentioned in the Bible. The Jewish law commanded the people to season the meat offering with salt (Lev. ii. 13). The Jews used a very impure argillaceous kind of rock salt, from which they extracted the salt by means of water, leaving the clay as mud. This mud still contained some salt, and was either used directly for agricultural purposes, or was allowed to lie on the manure heaps before being used, where, after prolonged exposure in presence of nitrogenous matter, the salt was partially converted into sodium nitrate. Hence we find the expressions (Matt. v. 13), 'Ye are the salt of the earth: but if the salt have lost his savour, wherewith shall it be salted? it is thenceforth good for nothing, but to be cast out and trodden under foot of men'; and (Luke xiv. 34) 'Salt therefore is good: but if even the salt have lost his savour, wherewith shall it be seasoned? It is fit neither for the land nor for the dunghill: men cast it out.'

Occurrence of salt. Salt is very widely distributed. Immense deposits of it, in the form of rock salt, are found in many parts of the world. It is the principal solid constituent of sea-water and of many salt lakes, and is found in brine springs and most mineral waters. There are few countries in which it does not occur, as also there are but few geological formations from which it is absent. In America rock salt is met with in very old strata, some of the recent discoveries of it being in the Silurian rocks.

In New York State, Michigan, and in Ontario it is found in the Upper Silurian formation, and usually lies at a depth of over 1000 ft. from the surface. South of Rochester (New York), in what is known as the Warsaw district, the rock salt is found in three superposed beds. The top layer is 60 ft. thick; then follows 10 ft. of shale. The second bed is 20 ft. thick, and is separated from the third by 30 ft. of shale. The Ontario deposits are found in the counties of Essex, Lambton, Middlesex, Huron, and Bruce lying along the shores of lake Huron. The beds are struck at depths varying from 970 to 1650 ft., and in some places they reach a thickness of 250 ft.

Rock salt is also known in Manitoba and Athabasca (*see* Geology and Economic Minerals of Canada, Depart. of Mines, Ottawa, 1909).

The rock salt found in Michigan is principally at Saginaw, Detroit, and Bay City. In Utah there are extensive deposits embedded in red clay. Salt is also found in Virginia, Ohio, Louisiana, and Kansas. The deposits which occur in Louisiana lie in the post Tertiary formation, while those of Kansas are found in the Permian. The latter have been proved to be most extensive, reaching into Oklahoma.

Rock salt is known in Mexico, Colombia, Venezuela, and the Argentine. There are immense deposits in Chile and Peru. It is found at Kulpi in Armenia, at Nachitschevan, and in many places in the Caucasus. It is claimed that the rock salt deposit near the town of Iletz Zaschtchiti in the province of Orenburg, S.E. Russia, is the richest in the world (Chemical Trade Journal, Feb. 1910, 179).

The district of Ferghana Turkestan is rich in salt deposits. Rock salt is widely found throughout the basin of the river Donetz in southern Russia, and at Vsolje where it occurs in Oolitic limestone. It is also known at Balachna on the Volga and in the Crimea.

On both sides of the Carpathians rock salt abounds, most of it in Tertiary formations. In Galicia the principal mines are at Wieliczka (where the deposit is said to be 1200 ft. thick), at Stebnick (where three beds have been found), and at Bochnia. Transylvania and Wallachia possess many mines. In the Tyrolean Alps rock salt occurs in Oolitic limestone. In the Austrian portion, the principal deposits are at Salzburg, Aussee, Ischl, Hallstadt, and Hallein; while in Bavaria, salt is found at Berchtesgaden and Reichenthal, and in Hungary at Marmores. At Volterra, in Italy, there are several deposits at 150–308 ft. from the surface.

In Spain rock salt is plentiful; but the most remarkable deposit is that of Cardona (Barcelona), where there are two hills of very pure white salt, each about a mile in circumference.

Germany is rich in salt. The principal formations are those of Stassfurt which lie in the Bunter sandstone, and are first reached at about 832 ft. from the surface. The salt is here accompanied by beds of potassium and magnesium salts (*see* POTASSIUM).

Salt is also found at Heilbronn in Würtenberg, Wimpffen in Hesse, and Rappenau in Baden, at Langenberg and Köstritz in Central Germany, at Gera in Reuss, at Buffleben in Coburg Gotha, and at Artern in Prussia.

Deposits are found in the Vosges district at Dieuze and Vic in Lorraine, and near to Nancy in France in Keuper marls. Switzerland possesses salt at Bex in the Rhone valley found in the Lias.

The Pyrenees are rich in brine springs and rock salt deposits. The beds of Dax and Villefranche are probably Tertiary. At Jebel Usdum, south of the Dead Sea, there is a hill which consists throughout of a single mass of rock salt, covered with a thin layer of calcareous marl. Salt is found in Algeria in cretaceous rocks, and in Abyssinia. In the interior of Libya it is found associated with limestone in cliffs. Herodotus mentions five mountains which lie about equal distances from one another, across a tract of country 10 days' journey in extent (*see* H. B. Tristram, The Great Sahara, 72).

Rock salt is found in India in the red marls and sandstones of the Devonian group. The salt range of the Punjab contains hills of very pure salt and runs across the districts of Jhelum and Shakpur from the bank of the Jhelum river to Kalabagh in Bannu district. Similar deposits are found in Kohat and Mandi.

In China the salt bed is a triangular tract having the Min river from Ching-ting-fu to its junction with the Yangtze at Sui-fu for its base, and its apex near Tzelintsing an area of some 1500 square miles.

The first discovery of rock salt in the British Isles was made at Marbury near Northwich in Cheshire in the year 1670.

In 1779 it was found at Lawton in Cheshire, and deeper borings at Marston in 1781 revealed the existence of a second or lower bed of salt. These Cheshire beds lie in the Saliferous marls of the Upper Trias formation above the New Red Sandstone, probably identical with the Keuper marls and Bunter sandstone of Germany. At Northwich the top bed is about 75 ft. thick, and lies 135–150 ft. below the surface. It is covered by boulder sands, clays, and red or blue marl. Below the top rock salt there is a bed of hard marl 30 ft. thick, which contains here and there veins of salt and masses of gypsum. Under this a second bed of rock salt is found about 105 ft. thick. Deeper borings reveal the presence of successive thin beds of salt. At Marston near Northwich the Salt Union drilled a borehole 2610 ft. deep, starting at 77 ft. above ordnance datum, and found a bed of salt 90 ft. thick at 124 ft., then 28 ft. of marl, succeeded by rock salt 92 ft. thick. Below this they found marl and thin beds of salt for 966 ft., and then passed through sandstone and marl or pure sandstone for 1310 ft.

A borehole over 2000 ft. deep is reported to have been drilled recently at Holford (3 miles east of Marston) that has shown the existence of beds of rock salt 1027 ft. from surface, aggregating 503 ft. thick.

At Winsford in Cheshire the beds are similar to those at Northwich, the top rock being about 70 ft. thick and the bottom 120 ft. Rock salt is also found in Cheshire at Sandbach and Lawton. At Droitwich and Stoke Prior in Worcestershire the salt beds lie in the same formation as in Cheshire. At Shirley Brook, in the same county, rock salt is found 273 ft. below the surface. It is met with at the village of Preesal, near Fleetwood in Lancashire, at a depth of 278 ft. (*see* Thompson, Trans. Manchester Geol. & Mining Soc. 30, 105), and is also found near to Barrow-in-Furness and in the Isle of Man at the Point of Ayre at 617 ft. below the surface (*see* Dawkins, Quart. Jour. Geol. Soc. 58, 1902). At Stafford Common in Staffordshire it is 263 ft. deep. In the neighbourhood of Middlesbrough, in the county of Durham, rock salt has been proved to exist over an area of 20 square miles. The most northerly bore-hole is at Greatham, where salt was found at a depth of 889 ft. below sea level. To the south, at North Ormesby, in Yorkshire, the bed is 1340 ft. from the surface, while the most easterly bore-hole at Lackenby strikes the salt at 1685 ft. (119 ft. thick), and the most westerly one at Haverton Hill reaches it at 797 ft. The average thickness of the main bed of salt is 84 ft. It lies in marls below a thick bed of red sandstone (*see* Durham Salt District by E. Wilson, Quart. Jour. Geol. Soc. Nov. 1888; also John Marley on the Cleveland and South Durham Salt Industry, N. of England Inst. of Mining Engineers, 1892, 27). Rock salt is found at Duncrue and Eden near Carrickfergus, and at Magheramorne near Larne in Ireland.

Origin of rock-salt deposits. The great variability in the position of the salt deposits renders it impossible to consider them as constituting a definite geological formation, but points to the probability that their origin is due either to volcanic action or to the evaporation of water which held the salt in solution. The great argument in favour of an igneous origin rests upon the fact that sodium chloride and hydrochloric acid are emitted by volcanoes; but the occurrence of layers of bitumen and certain organic remains, together with the fact that cavities containing liquids are found in the rock salt, renders this theory untenable.

The general character of the beds, too, favours the assumption that they are of aqueous origin. They are rarely found filling cavities or dykes after the manner of volcanic rocks, but are in layers of very considerable area. These immense beds of rock salt most probably owe their origin to the evaporation of inland seas, and a careful examination of their constitution affords evidence which goes far to prove this theory. The manner in which the deposits were formed appears to be as follows. When, by slow upheaval of the land or by the accumulation of a bar or sand bank, a portion of the sea became partially shut off, the heat of the sun was sufficient to evaporate as much water as was supplied by the sea or by rivers.

Then the volume of water in the part so separated became gradually richer in dissolved salts. The upper layers when concentrated by the sun became specifically heavier and sank to the bottom, the more dilute rising to take their place. As the quantity of salt in solution rose, all those living organisms which were endowed with the means of locomotion left their homes and returned to the open sea, while those which were lacking in this particular died off. Their remains (such as did not dissolve) are found as insignificant impurities in the gypsum which formed around them. For by degrees the lower portion of the water became so rich in mineral constituents that it could no longer retain them in solution, and they began to separate out. The least soluble salt was, of course, the first to deposit, and this was followed by the others in the inverse order of their solubility. The calcium carbonate and ferrous carbonate, if present, would precipitate first, and then the calcium sulphate would follow in the form of gypsum. As the degree of concentration still continued to rise the sodium chloride began to separate out, depositing on the bottom of the basin in a hard compact mass. In cases where the connection with the sea was still maintained, or where rivers continued to send in water, these various phases would be to a certain extent contemporaneous; for the incoming water would bring with it fresh quantities of calcium carbonate and calcium sulphate, and these salts would precipitate along with the sodium chloride. Nor would this separation of the salts in the inverse ratio of their solubilities proceed with absolute exactitude, for the less soluble might carry down with them minute quantities of the more soluble ones. For instance, it is by no means uncommon to find magnesium sulphate mixed with rock salt, especially where there has been aluminous mud washed in to serve to carry it down. Again, certain combinations of the same salt occur, such as *simonyite*, and *bischofite* is found in solution in cavities in rock salt in Cheshire, where also *hydrophilite* is not infrequently found. As the sodium chloride continued to deposit, the mother liquor gradually grew richer in the more soluble salts until the point was reached when they too began to crystallise. Potassium chloride and magnesium chloride separated from the solution in combination as the mineral *carnallite*. Potassium sulphate, magnesium sulphate, and magnesium chloride became associated as *kainite*, while some of the magnesium sulphate crystallised in the form of *kieserite*.

It is obvious that when the supply of fresh water from the ocean was continued at all there would be a deposit of salt accompanying the more soluble substances. The calcium sulphate, however, which precipitated from this sea water would, in falling, pass through the layers of mother liquor which had reached a high degree of concentration; hence it crystallised as *anhydrite*. The whole of this process of crystallisation was, of course, subject to an immense variety of disturbing influences. The rate of deposition would vary greatly with the season of the year, not only on account of the heat of the sun and the height of the tides, but also on account of the amount of water due to the rainfall. There were probably actual changes in climatic conditions giving at one time a tropical heat and rapid deposition of salt, and at another copious rainfall which arrested crystallisation and caused the rivers to bring down plentiful supplies of mud. In examining beds of rock salt we find evidences of such disturbances in the frequent occurrence of layers of clay, sandstone, or marl, which show that during certain periods there was little or no deposit of salt. In many cases the disturbance was sufficient to remove the whole of the mother liquors, and there we find little or no trace of the potassium and magnesium salts.

Such is the generally accepted theory of the formation of the great deposits of rock salt. The ocean has for ages been receiving the waters of rivers and springs charged with matter dissolved during the passage of the water through or over the various rock formations. Such substances as were required to build up the structure of marine animals and plants were by them extracted from the water; the rest would obviously, in course of time, accumulate, because the volume of sea water was kept nearly constant by continual evaporation.

Such formation of salt deposits may be seen proceeding at the present time, two of the best examples are afforded by the Kara Boghaz or Black Gulf on the eastern shore of the Caspian Sea and the Runn of Cutch in India (*see* Thos. Ward, Trans. Manchester Geo. Soc. 18, 396; Riemann, Monographien über Chemisch-technische Fabrikations-Methoden Band, xviii.; Halle, 1909, 8).

Rock salt. Rock salt is always found in England associated with a coloured marl, and through having undulating lines of this impurity running through its mass, it generally presents the appearance of stratification.

The tinge of colour varies with the colour

COMPOSITION OF ROCK SALT.

—	Cheshire	Wieliczka, white	Vic, red	Vic, grey	Hall, Tyrol	Marennes red	Virginia	Algeria	Berchtes-gaden	Schwäbisc, Hall	Wilhelms-glück	Holsten, U.S.	Stassfurt	Cardona
Sodium chloride	98·30	100·00	99·80	90·30	99·43	96·78	99·55	99·30	99·85	99·63	98·36	99·55	94·57	98·55
Calcium chloride	—	—	—	—	0·25	—	trace	—	—	0·09	—	—	—	0·99
Magnesium chloride	0·05	—	—	—	0·12	0·68	—	—	0·15	0·28	—	—	0·97	0·02
Sodium sulphate	—	—	—	2·00	—	—	—	—	—	—	0·03	—	—	—
Calcium sulphate	1·65	—	—	5·00	0·20	1·09	—	0·50	—	—	0·55	—	0·89	0·44
Magnesium sulphate	—	—	—	—	—	0·60	—	—	—	—	—	—	—	—
Calcium carbonate	—	—	—	—	—	—	—	—	—	—	0·52	—	—	—
Magnesium carbonate	—	—	—	—	—	—	0·45	—	—	—	0·13	0·45	—	—
Alumina and ferric oxide	—	—	—	2·00	—	0·85	—	0·20	—	—	0·53	—	3·35	—
Water	—	—	0·20	0·70	—	—	—	—	—	—	—	—	0·22	—
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·12	100·00	100·00	100·00

of the marl and marlstone with which it is interstratified. It varies from dark red or brown to light amber or white. The yellow rock salt is preferred, on account of its greater purity. The table on p. 9 shows the composition of the salt obtained from deposits in various parts of the world.

The Cheshire salt mines which are now being worked are all in the lower bed. The rock obtained is purer than that from the upper one, and there is less trouble required to keep out surface water and brine. The modern mine is provided with two shafts placed from 10 to 15 yards apart, with generally (unless the winding shaft be tubed) another permanent shaft for pumping the surface water, sunk only as deep as the water penetrates. In sinking the shaft it is especially requisite to protect the rock salt at the sides from being dissolved by water. All such shafts are roofed over to keep out rain and snow, and are carefully cased down to a solid foundation below where surface water penetrates in the ground. The casing was originally made of wood; but lately this has been replaced by iron. The method of procedure in Cheshire is as follows:—

A solid foundation, such as is generally to be found at a certain bed of marlstone between the top and bottom beds of rock salt, is obtained, and then a ledge 12 ins. wide all round is cut in it, care being taken to remove any small concretions of rock salt which may be in the marl. A bed of concrete is cast upon this ledge and carefully dressed on the surface to receive a cast-iron ring. The bottom length of tubing (called the bell mouth) is generally about 6 ft. long, and is in three segments which, when united, taper from a diameter of about 4 or 5 ft. at the bottom to 3½ ft. at the top, and on this begin the iron cylinders or tubes 3½ ft. diameter and 6 ft. long. The space behind the bell-mouth is carefully filled with cement rammed well down to the concrete foundation.

In the bottom bed workings the height of the rock salt that is being worked varies from 15 to 18 ft. in Cheshire, and from 30 to 40 ft. at Carrickfergus. The mode of working the mines in both districts is to drive out in the upper part about 5 ft. 9 ins. high, which is called the 'roofing,' and to follow up with what is called the 'benching,' leaving pillars of rock salt to support the roof. In driving the roofing a little holing and cutting has to be done with a pick, and as much as possible is blown out with gunpowder, after which the roof is dressed off with a pick. The benching in Cheshire varies from 9 ft. 3 ins. to 12 ft. 3 ins. in thickness, and in Ireland from 24 ft. 3 ins. to 34 ft. 3 ins. This is blown off by a succession of shots, arranged in a slanting direction from the top to the bottom. In some of the mines machines are used. In charging the shot the fine rock salt made in drilling the hole is put next to the powder and coarse-grained rock salt upon that. The stemmers and prickers are all made of iron, as rock salt does not strike a light with iron or steel.

Flat hemp ropes are generally used for winding. In some cases iron-wire rope is used, but it has to be kept well greased to prevent it rusting. Tram roads are used below ground. It is found by experience that the pillars which are left to support the roof should be in proportion to the depth of the mine. At a depth of 330 ft. it is found necessary to leave 1 pillar for every 11½ times its area of rock worked. The pillars are left 10 yards square, and stand 25 yards apart. There is a crushing and grinding mill at the bank of nearly every rock-salt pit, and in this the rock is ground to more or less fine powder when so required for shipment (*see* V. Buschman, Das Salz dessen Vorkommen und Verwertung, Willhelm, Engelmann, Leipzig; also F. A. Fürer, Salzbergbau und Salinenkunde, Vieweg und Sohn, Brunswick).

The rock salt which is found in the neighbourhood of Stassfurt, in Prussia, is accompanied by deposits of a great variety of other minerals, especially those rich in potassium and magnesium. After boring through the Bunter sandstone, a bed of red clay and gypsum is encountered, under which lies the upper layer of rock salt, varying in thickness from 150 to 300 ft. For particulars of Stassfurt deposits *v.* POTASSIUM, vol. iv. p. 337.

The salt deposits in the districts of Tarapaca and Atacama, in Chile and Peru, in great measure resemble those of Stassfurt. There is, however, one remarkable point of difference—the Peruvian beds contain large quantities of sodium nitrate or Chile saltpetre. The source of this nitrogen has long been a matter for discussion; but recent researches afford most probable explanations of its origin. It is noticeable that all these 'calichales' or 'salitrales,' as the spots are called where the 'caliche' or impure soda saltpetre is found, lie near to the coast, just inside the low-lying coast Cordilleras. The coast in this part of Chile is studded with small islands containing deposits of guano rich in ammonia, and this (in the form of very fine dust) is carried by the prevailing west wind far inland, and would doubtless fall into the saline lakes when in process of evaporation. The oxidation of this nitrogenous matter would doubtless readily take place under such climatic conditions as obtained when the salt deposits were formed.

The greater prominence of the more soluble potassium and magnesium salts in the nitre-bearing Chilean deposits furthers the supposition that they were formed from mother-liquors decanted from salt lakes further inland by volcanic upheaval. The theory that these mother-liquors, running down to the sea, were intercepted by the coast mountains is borne out by the fact that where there are no hills along the shore there are no nitre beds.

Manufacture of salt from brine.

The manufacture of salt has been carried on in England since the time of the Romans, who, there is little doubt, made it from brine. Brine is formed by fresh water reaching the surface of the rock salt, either at the outcrop of the strata or through a fissure in the overlying marl. In Cheshire it is pretty certain that the water gains admission at a higher level than the rock salt, for when the brine is first struck it rises up the shaft to a considerable height, in some cases nearly to the surface. The natural brine is, as would be supposed, only found on the top of the upper beds of rock salt. It is reached by sinking a huge well or shaft, sometimes as much as 10 ft. in diameter. For the purpose of keeping water out, the shaft is lined with cast-iron cylinders carefully jointed together (see description of rock-salt mine shaft), or with timber backed with puddle. This shaft is carried down until the marl is reached, and then a bore-hole is driven until the brine is tapped. The top bed of rock salt in Cheshire is usually covered with a bed of marlstone, locally called 'the flag,' which is very hard and impervious to water. For a few feet below the flag the marl in which the rock head brine runs is of a granular structure, locally known as 'horse beans' or 'shaggy metal,' and is probably the remains of marl or other impurity originally combined with the rock salt, but left behind as the rock salt is dissolved into brine. On piercing the flag the brine rises into the shaft with great force. Common lift pumps are employed to raise the brine to the surface. They are suspended by a chain of rods depending from a rocking shaft or R bob at the top of the well. One engine, placed near the top of the shaft, generally works a pair of pumps. The brine is delivered into reservoirs which are lined with puddle-clay and brickwork.

The clay suffices to make them watertight, and the bricks, which are laid without mortar on the top of the puddle, keep it from being washed away. Very frequently, large wooden tanks are used as brine reservoirs. These are constructed of stout planks held together by wooden plugs (nails cannot be used on account of corrosion) and carefully caulked with oakum. The brine is distributed to the salt pans through pipes. In many places it is common to employ pipes made out of the trunk of a tree bored out in the core and tapered at one end. The taper end fits into the core of the next pipe.

Such ranges are found to stand changes of temperature better than iron ones. In Austria also there are many miles of such ranges of pipes. The strength of brine varies very greatly. It is, of course, dependent upon the volume of water which passes over the rock salt, the area of the surface over which it runs, and the length of time it is in contact with it. The table on this page shows the composition of brine in various places and countries.

In some countries where the brine is found too weak to make the ordinary method of evaporation a profitable one, recourse is had to a device to strengthen the brine by evaporation at the ordinary temperature. This is done by means of so-called graduation towers or houses (German, *Gradirhäuser*). They consist of scaffolding which incloses bundles of brambles or thorns, built up in regular walls. The weak brine is pumped up to the top, and carefully distributed by means of perforated troughs all over the summit of the pile. It then falls from twig to twig, and is divided into a fine shower on its way to the ground, thus exposing an immense surface to the action of the air or wind. At the bottom it falls into a collecting trough, whence it is returned to the top of the same or another tower until it becomes sufficiently concentrated. In time, the thorns become coated with a scale of calcium carbonate and sulphate, and then they have to be renewed. This incrustation is technically known as thorn-stone (German, *Dornenstein*). The graduation houses should

COMPOSITION OF BRINES.

100 parts of brine contain	Marston	Wheelock	Droitwich	Stoke Prior	Friedrichshall	Hall	Artern	Clemenshall	Sulz	Syracuse, New York, U.S.A.	Stafford	Fleetwood	Middlesbrough	Winsford	Middlewich	Northwich Bottom Mine	Schönbeck	Rodenberg
Sodium chloride .	25·222	25·333	22·452	25·492	25·563	25·717	25·267	25·902	23·473	21·710	24·850	24·980	24·930	25·460	25·110	25·790	9·623	5·173
Potassium chloride	—	—	—	—	—	—	0·119	—	—	—	—	—	—	—	—	—	0·007	—
Magnesium chloride	—	0·171	—	—	0·005	—	0·421	—	—	0·136	0·168	0·046	—	0·214	0·171	0·093	0·083	0·166
Calcium chloride .	—	—	—	—	—	—	—	—	—	0·188	—	—	—	—	0·053	0·044	—	—
Potassium sulphate	—	—	—	—	—	—	0·291	—	—	—	—	—	—	—	—	—	0·014	0·515
Calcium sulphate .	0·391	0·418	0·387	0·261	0·437	0·171	0·400	0·444	0·508	0·505	0·429	0·515	0·450	0·452	0·425	0·450	0·339	—
Sodium sulphate .	0·146	—	0·390	0·594	—	0·038	—	0·019	—	—	—	—	0·020	—	—	—	0·249	0·005
Magnesium sulphate	—	—	—	—	0·023	—	—	—	—	—	0·090	—	0·046	0·001	—	—	0·012	0·010
Calcium carbonate	—	0·052	—	—	0·010	0·002	—	0·019	0·016	—	0·010	0·036	0·030	0·016	0·004	0·018	0·026	—
Magnesium carbonate	0·107	0·107	0·034	0·034	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ferrous carbonate	—	—	—	—	—	—	—	—	—	0·005	—	—	—	—	—	—	0·001	—
Total . .	25·866	26·081	23·263	26·381	26·038	25·928	26·498	26·384	23·997	22·545	25·547	25·577	25·476	26·143	25·763	26·395	10·354	5·869

be built lengthwise in the direction of the prevailing wind. The rapidity of evaporation depends upon the hygrometric state of the atmosphere. On rainy days graduation cannot go on. Experience shows that from May to August is the best season. It has been calculated that in ordinary good weather 60 kilos. (13 gallons) of water are evaporated in the course of 24 hours for every square foot of surface of the thorns. This method of evaporation is employed among other places at Moutiers in France, and at Nauheim, Dürrenberg, Rodenberg, and Schönbeck in Germany.

In some districts where rock salt is found the water does not naturally percolate to the strata, and therefore no brine is struck when borings are made. An artificial brine is readily prepared by turning a stream of fresh water down on to the bed of salt, and then pumping it up again as it becomes saturated with salt. The strong brine, being much heavier than water, collects at the bottom of the shaft, so the pumps are made to draw from the bottom, and are only run so long as the brine delivered keeps up to strength. The yield of such a brine shaft, of course, depends upon the area of the surface of the rock salt which the water can act upon, and this it will be seen is always increasing. The whole of the brine evaporated in the Middlesbrough district is made in this way. Water from the sandstone strata is allowed to flow down the well outside the pump barrels, and thus solution of the salt takes place at the top of the bed, by which a cavity is formed. As the brine is pumped from the bottom of the cavity more water flows down, and thus the cavity becomes larger and its productive power is increased. As the specific gravity of brine is about 1·2, the column inside the suction pipe rises to ⅚ of the height of the water column outside.

The removal of these subterranean beds of rock salt by the agency of water occasions in some districts very serious consequences. In carefully worked mines the pillars which are left are ample to support the superincumbent strata so long as the mine is kept dry. But if, by any chance, water finds its way in large quantities into a salt mine the pillars are rapidly dissolved, and a large area of roof is left without any support. Then a subsidence of the land, occurring more or less rapidly, is sure to take place. The water which finds its way down to the rock-salt beds may run for miles along its surface, and so gradually remove an ever-increasing layer of the salt. If there is no natural outlet the solution of salt ceases when the water becomes saturated; but if the brine is pumped out for manufacturing purposes an equivalent volume of fresh water is induced to flow in, and so the destruction of the salt bed is greatly intensified. This constant removal of the support causes as constant a subsidence of the outlying lands, and it is by no means uncommon in the brine-pumping districts for pieces of land to sink at the rate of a foot a year (*see* Subsidences in the Salt Districts of Cheshire; their History and Cause, Thos. Ward, Trans. Manchester Geol. Soc. vol. xix., part vii. 1886–7).

The manufacture of salt from brine is essentially a very simple process. It is merely necessary to evaporate a certain amount of water and collect the salt which deposits. This is effected either by artificial heat or by the heat of the sun. When the former is employed, it is obvious that the best process is that which secures the greatest evaporation for the smallest expenditure of fuel. Until recently, the method universally adopted was to use an open shallow pan and heat it by a fire placed underneath. The Romans in Cheshire used leaden pans which contained only a few gallons of brine; but the modern pans are made of wrought iron plates riveted together and frequently hold as much as 50 cubic metres. Apart from this variation in the construction and size of pans, the process has been little affected by the various and numerous patents taken out for improvements until about 1892.

The following is a list of some of the most important of the patents:—

In 1764 John Baker patented a salt-pan covered over from end to end with a brickwork arch, and so arranged that the hot gases which had already passed under the pan should be drawn over the surface of the brine.

In 1772 Daniel Scott and John Mackay proposed to arrange pans three high, and conduct the steam from the bottom boiling pan through false bottoms under the other two.

In 1801 James Manly patented a process for purifying brine. He proposed to heat, in order to remove part of the impurity, and then to add sodium carbonate to it.

In 1806 Richard Tomkinson designed a salt-pan which contained a hollow iron cylinder running right down the centre and out at the other end. The middle of the pan was deeper than the sides, and the cylinder was supported so that the brine surrounded it at all times. The fire was placed in the cylinder at one end of the pan.

In 1808 William Steel patented a plant consisting of three separate vessels. The boiling vessel was provided with an air-tight cover, and the steam from it was conducted under a second vessel. The hot air and flame from the flue of the first was taken under a third vessel.

In 1824 W. A. Jump and W. Court proposed to heat the first brine in metallic pipes, placed in the flues under the pan.

In 1831 W. A. Jump patented a pan provided with mechanical rakes to draw the salt to the side of the pan.

In 1833 W. Newton proposed to blow hot air through the evaporating brine.

In 1838 Joseph Hall patented a circular revolving pan. The salt, as it formed, was scraped by means of a fixed rake into a pocket at the circumference of the pan. He also described a semicircular pan with a reciprocating motion. He claimed that in such pans the heat was more evenly distributed and the wear consequently less.

In 1839 Edward Law patented a machine for evaporating brine by exposing an extensive surface to the action of a brisk current of air. The apparatus consisted of an upright shaft or axis carrying ten frames covered with canvas. These were constantly moistened with brine while the machine was turned rapidly on pivots.

In the same year (July 16, 1839, No. 8155) an important step was taken by John Reynolds, who invented a process for improving the manufacture of salt by 'causing the steam produced by boiling brine or salt water in a closed vessel to transfer its heat to and thereby boil brine or salt water in a second closed vessel, so that the steam from such second closed vessel may in like manner transfer its heat to brine in a third vessel, and so on, by maintaining in each of a series of closed vessels in which brine is subjected to evaporation such relative pressure as will cause the respective boiling-points of the brine contained in each to be lower from the first to the last of the series, so that the steam or vapour produced from the brine in each vessel may be condensed in a vessel of thin metal immersed in the brine of the next succeeding vessel. The graduations of pressure may be obtained either by diminishing a pressure superadded to that of the atmosphere, or by diminishing the pressure of the atmosphere alone.'

In 1855 L. J. F. Margueritte proposed to precipitate salt from a solution by passing hydrogen chloride into it.

In 1864 D. Hall and A. L. Roosen patented the application of surface heating for the evaporation of brine. The pan was covered with a brick arch, and the heat from the furnace was allowed to pass over the surface of the brine, and then afterwards, together with the steam evolved, under an ordinary open salt-pan.

In 1889 Alberger, Williams and Alberger patented a combination of tubular steam heaters and a circular open pan termed a 'grainer.'

In 1893 C. Hirzel proposed to freeze brine at −20° and separate the hydrate.

In 1898 Vis patented the use of calcium chloride to prevent the calcium sulphate in brine scaling a pan.

In 1899 Vis patented an arrangement for preventing scaling in vacuum apparatus.

In 1899 Duff patented a special arrangement of multiple effect vessels.

In 1900 Vis proposed the purification of brine by electrolysing it until caustic soda was formed in sufficient quantity to precipitate the calcium and magnesium salts when treated subsequently with carbon dioxide.

In 1902 Sachse and Kaufmann patented apparatus for keeping the tubes of a vacuum evaporator clear by causing a weighted chain to bump over the top tube plate.

In 1903 Trump took out a patent for vacuum apparatus containing a circulating pump which, by causing the crystals and mother liquor constantly to be returned to the evaporator, allowed the crystals to grow larger and at the same time tended to prevent the formation of scale by scouring action.

In 1903 Tee patented a process for making white salt by melting rock salt, blowing heated air through the liquid, allowing impurities to settle and then drawing off the clear salt into vessels to cool.

In 1908 Malcolm and Munton patented a process for preventing scaling in vacuum evaporators by purifying the brine. The magnesium salts are removed by adding partially electrolysed brine (*i.e.* brine containing some caustic soda) to the raw brine and then the calcium salts are precipitated by the addition of more electrolysed brine and treatment with flue gases (*i.e.* CO_2).

Of late years the greatest improvements which have been made in the manufacture of salt have been in the direction of the triple effect apparatus described by Reynolds in 1839.

The cost of fuel is so large an item in the cost of production of salt that any economy effected in its use materially increases the margin of profit. With the ordinary open pans, 1 ton of fuel (slack with 15–20 p.c. of ash) will make from 2 to 2·5 tons of salt; but a well constructed triple effect plant will yield 5–6 tons of salt per ton of fuel. In addition to giving greater economy in consumption of fuel, these vacuum pans have a much larger production capacity than the ordinary pans.

While, with a direct-fired pan of large size, it is considered good to get 15 tons of salt per 24 hours, it is not uncommon for a set of multiple effect vacuum evaporators to yield 500 tons per day, and some are now being built to produce 720 tons per set of three vessels. The evaporators are constructed with a central heating portion, a dome-covered upper part and a conical lower portion communicating with a salt receiver.

Heat is applied to the vessels through tubes which prevent the brine from coming into actual contact with the heating medium.. Steam or any hot gases, such as flue gas or exhaust from gas engines, can be employed for heating the first vessel in the series. The steam which is evolved from the boiling brine in the first vessel is employed for heating the second of the series, and that from the second serves to heat the third. Where a fourth vessel is employed, the heating is effected by steam from the third. The steam evolved from the last vessel of the series passes to a vacuum engine either direct or after a condenser. With this arrangement, evaporation takes place in each vessel at a lower pressure, and therefore at a lower temperature, than in the preceding vessel, so, while the pressure in the first may be little below atmospheric, that in the last is a high vacuum.

To facilitate the removal of salt without interruption of the process of evaporation, it is usual to make a long leg to the evaporators so as to maintain a column of brine equal to the vacuum and allow the crystals to fall into a receptacle which lutes the bottom of the leg. It is common to provide this with an elevator and so remove the salt as it forms to a storage hopper.

Fig. 6 shows the arrangement of a typical multiple effect plant. In this plan (copied from a recent patent) four vessels are shown, marked A1, A2, A3, and A4. The heating chambers are marked B1, B2, B3, and B4. That of B2 is shown in part section to illustrate the arrangement of tubes through which the brine circulates. The long legs C of each pair of vessels meet in one boot at an elevator bottom, and the salt is raised by the elevators E to the receptacle F. G is a condenser for producing vacuum by the condensation of steam.

Fig. 7 shows an end view of the same plant. Each vessel has a separate brine-feed pipe from a common main.

Fig. 8 (p. 15) illustrates another form of plant where the vessels are placed at different heights, so as to give a length of leg in proportion to the vacuum in the vessel. Here each evaporator has its own elevator.

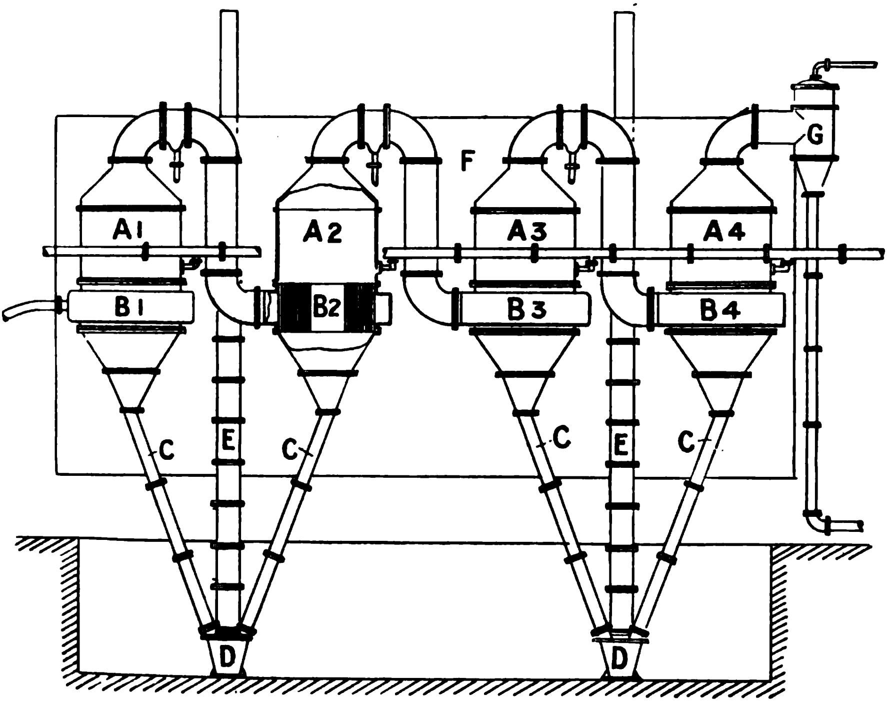

FIG. 6.

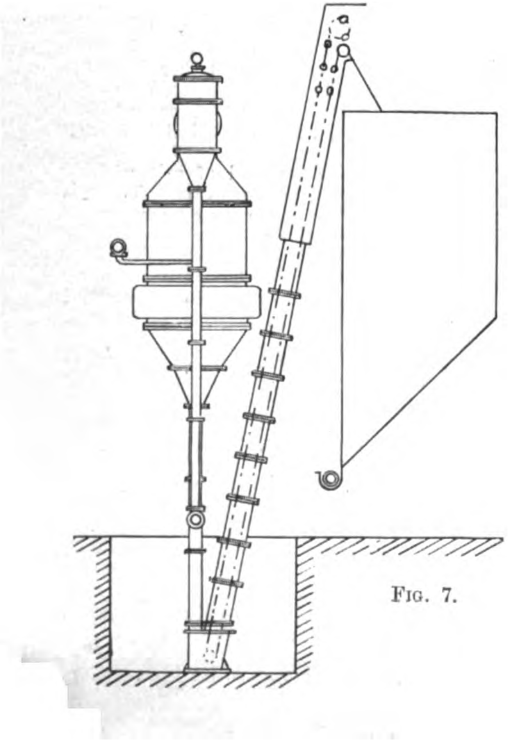

FIG. 7.

This process has rendered the manufacture of salt remunerative in places where heat was in some form or other being wasted. One of its first applications was in utilising the exhaust steam from the lumber mills of Michigan, and latterly it is being found suitable for making use of the steam from turbines and for generating electricity. The great source of trouble in working the process is the impurity of ordinary brine. The calcium sulphate, which every natural brine contains, separates in the form of scale on the tubes. This scale, containing anhydrite and a large quantity of salt, has to be constantly removed because it seriously interferes with the transfer of heat.

Many devices have been tried to overcome this difficulty. Some of the most obvious are those which deal with the partial purification of the brine prior to its use in the evaporators. Other mechanical ones have been fairly successful, notably that patented by Trump in 1903. The best, however, appears to be the addition of calcium chloride to the brine during evaporation, as suggested by Vis in 1898. This causes precipitation of the calcium sulphate in the form of small crystals that mix with the salt and does not allow scale to form on the tubes. The salt, on withdrawal from the apparatus, is washed free from calcium chloride with fresh brine. The washings are sent with the brine fed into the evaporators and so the calcium chloride is used over and over again.

Salt makers experience one difficulty in working vacuum plant, and that is, the grain of the salt produced is always fine. Where a coarse grain of salt is required, brine which has been heated in a vacuum evaporator has to be allowed to flow through an ordinary open pan or a grainer so as to permit the crystals of salt to form slowly and to grow.

In the ordinary process of manufacturing salt the brine is run into a shallow pan, which is heated from below, and is made of such a shape as will expose as much surface as possible both to the action of the fire and of the air. The oldest pans of which there is any record were made of sheet lead, and were only about 3 ft. square and 3–4 ins. deep, holding little more than 15 gallons. These so-called 'leads,' when filled, were set aside in a warm place or on a hot flue, until the brine deposited its salt. About the middle of the seventeenth century iron pans superseded the leaden ones.

Writing in 1748, Brownrigg describes pans then in use as being made of 'plates of iron joined together with nails and the joints filled with a strong cement. Strong iron hooks hang down from beams of iron fixed across the pan and are linked to other hooks on the bottom of the pan and thus prevent it from bending down' (The Art of Making Common Salt).

In 1765 the largest pans used at Northwich were 20 ft. long by 9 or 10 ft. wide. At the present time the smallest employed are 25 ft. long by 20 ft. wide and 15 ins. deep, while some of the pans used for making coarse salt are 70 ft. long by 25 ft. wide and 18 ins. deep.

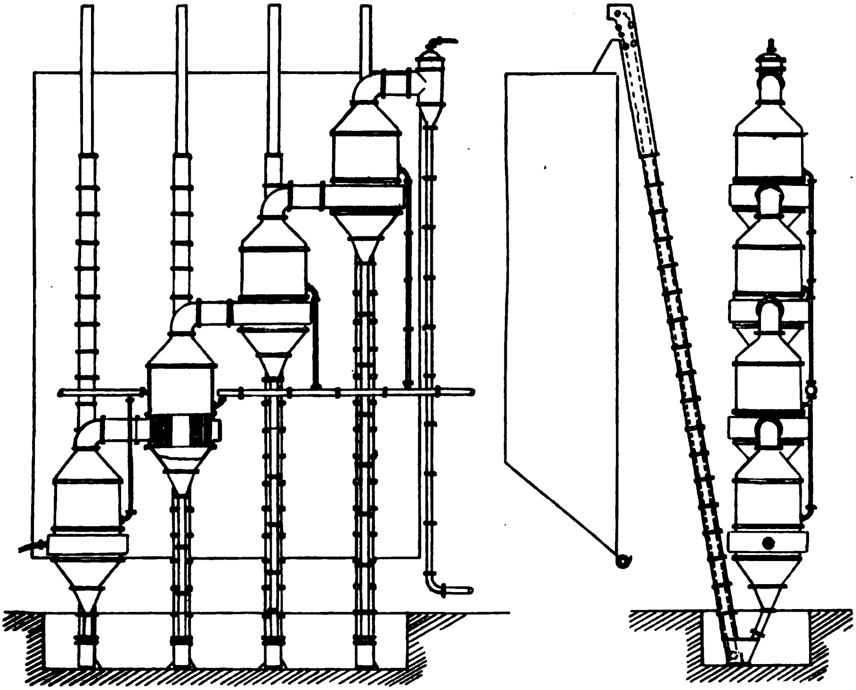

Fig. 8.

The pans are placed upon brickwork, which serves for a support and also forms the walls of the flues. The fireplaces are placed in the front, and vary in number from 2 to 4, according to the size of the pan and the work it has to do. The flues are frequently carried straight from front to back of the pan. In some pans the portions marked F in Figs. 10 and 12 are shut off from the flues in order that when the salt is raked up to the side, previous to drawing, it does not cause super-heating of the pan plates. Fig. 9 shows the front view of a salt pan; Fig. 10 is a cross section at the break shown in Fig. 11; Fig. 11 is a longitudinal section: Fig. 12 is a plan of the flues.

The pans are made of wrought-iron plates carefully riveted together like boilers. The plates which lie directly over the fires are made of greater strength than the rest of the pan, on account of the greater wear which they have to stand. As these plates have to be renewed more frequently than any others, they are made smaller, and are so arranged that they can readily be cut out (*see* Fig. 13). Each set of fire-plates A, A, A, A, is separated from its neighbours by a midfeather plate B, B, which rests upon the wall dividing two fireplaces. The two outer sets are separated from the side of the pan by a similar long plate. The bottom and sides of the pan are joined by means of an angle iron, to which each is firmly riveted (Fig. 14).

As above stated, the plates A which lie in the vicinity of the fires are subjected to the greatest wear. When they become over-heated they sink and stretch, and, in so stretching, they tear the plates C at the front of the pan. It is obvious that the removal of the front plate would necessitate frequent interference with the angle iron, and this would entail a greater expenditure of labour; therefore it is found advisable to place two rows of plates along the front. All the plates used in the neighbourhood of the fires are ⅜ in. thick, while those employed for the back parts are ¼ in. Some French pans have the fire-plates raised towards the centre above the level of the rest of the pan (*see* Fig. 17), in order that the salt, when formed, may float off the fire-plates. Salt-pans should be made to extend about 1 ft. or 1 ft. 6 ins. beyond the front wall, in order to keep the angle iron well out of the fires. They are also made to overlap the side walls by about 6 ins., for the double purpose of keeping the angle iron clear of the flues, and for allowing what is known as toe-room for the man who draws the salt out of the pan. If the drawer can place his toe under the pan, he is able to get his leg flat against the side of the pan. This affords him greater power in stooping over the pan, and prevents him wearing the skin off his knee. The best method of setting the pan on the side walls is to build up a 9-in. wall, and make the top course of bricks only 4½ ins. deep (*see* Fig. 15).

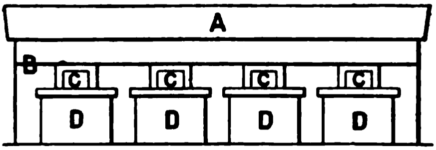

FIG. 9.—SETTING OF SALT-PANS.
A. The salt-pan. B. The front wall or fore-bye.
C, C, C, C. The fireplaces. D, D, D, D. Ash holes.

What is technically known as the 'standing side' consists of a gangway of 2-in. planks about 2 ft. wide, which runs the entire length of the pan, on a level with the top of the 9-in. side wall. On both sides of the pan, and often across the back, there runs a platform composed of 2-in. planks well jointed together, and caulked with oakum. These stages are technically known as the 'hurdles,' and serve for a receptacle for the wet salt freshly drawn from the pan. They have a fall towards the centre or half-length of the pan, and are bordered on the pan side by a gutter in order that the brine which drains from the salt may run back into the pan (Fig. 16). It is customary on the Continent to cover in the salt-pans with a wooden shelter, provided with an upright shoot to take off the steam. In such cases this cover serves instead of the hurdles, and it possesses the distinct advantage that the heat from the pan serves in a great measure to dry the salt. In some Continental works a tramway runs down the centre of this wooden cover, and the salt is taken off in trucks (*see* Figs. 17 and 18).

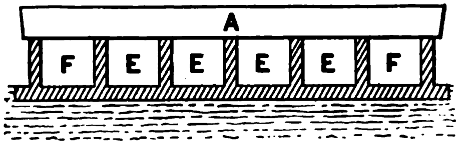

FIG. 10.—SETTING OF SALT-PANS.
A. The salt-pan. E, E, E, E. The flues.

Fine-grained or lump salt. Fine-grained salt is made in the smallest-sized pans. These are 25–35 ft. long and 20–24 ft. wide, and 15–18 ins. deep. The brine is boiled and reaches the temperature of 226°F. or 107·5°C. As the salt forms it is raked off the fire-plates to the side of the pan from time to time. Twice or three times in 24 hours the salt is drawn from the pan.

The salt is lifted out of the pan on a perforated sort of shovel, known as a 'skimmer' (Fig. 19). As it is drawn out of the pan it is placed either in wooden boxes (Fig. 20) standing on the hurdles, or thrown on to the hurdles in bulk. As it cools in the boxes the hot brine which it contains crystallises, and suffices to cement the whole together into a solid mass. This is knocked out of the box and placed in the stoving chamber to dry. This hot room is generally heated by the waste heat from the flues of boiling pans. The fine table salts are prepared by crushing and grinding the lumps after drying.

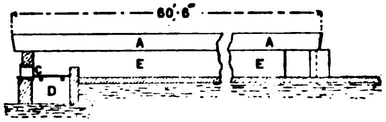

FIG. 11.—SETTING OF SALT-PANS.
A. The salt-pan. C. The fireplace. D. Ash hole.
E. Flue.

Common salt. The name 'common' is given to that grain of salt which is made for use in various manufacturing operations. It is made at a temperature of 160°–180°F., or 61°–82°C., in pans 45 ft. long by 25 ft. wide and 18 ins. deep. The salt is raked off the fires about every 2 hours, and drawn out of the pan every 24 or 48 hours. After draining on the hurdles for some hours it is shipped off in railway waggons.

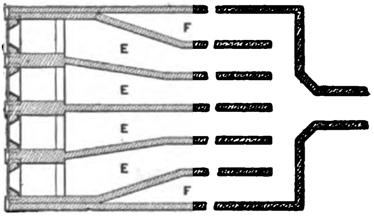

FIG. 12.—SETTING OF SALT-PANS.
E. Flues. F. Blank spaces.

Fishing salt. Fishing salt is a coarse-grained variety manufactured for the fish-curing trade. It is made at a temperature of 100°–140°F., or 37·7°–60°C., in pans 50–60 ft. long by 24–25 ft. wide and 2 ft. deep. The salt is drawn out once a week or once a fortnight, according to the grain required. These pans are often heated by the flue gases from boiling-pans. A little alum is added to the brine to harden the crystals of salt.

Bay salt. Bay salt is the coarsest-grained salt manufactured. The pans employed are very large, sometimes even 140 ft. long by 25–30 ft. broad. The temperature of the brine is kept at about 100°–120°F. The salt is drawn every 3 weeks or month.

The salt manufacturer frequently manipulates his brine in order to obtain the exact grain of salt that he requires. The addition of gelatin, glue, or any kind of grease causes the salt to form in very small crystals, whilst the addition of alum has the opposite effect. The operation of adding such substances is technically known as 'poisoning the pan.' Alum is employed in the manufacture of the variety of salt known as 'hopper salt.' It causes the salt to crystallise in hollow cubes, and as these float about before falling to the bottom of the pan they become surrounded by others, and gradually form into the shape of a shoot or hopper (Fig. 21).

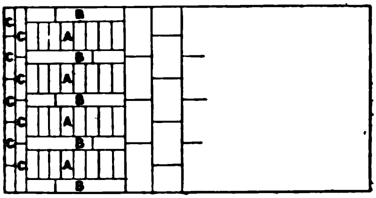

Fig. 13.—Plan of Salt-pan, showing Arrangement of Plates.

Natural brine is seldom a solution of pure sodium chloride, but generally contains other salts in solution, as will be seen from the foregoing analyses (p. 11). Certain of these substances separate out during the process of evaporation, and not only render the salt impure, but give trouble in the pan. If the brine contains calcium bicarbonate, the application of heat produces a precipitation of calcium carbonate.

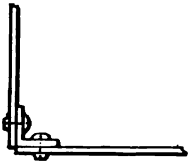

Fig. 14.

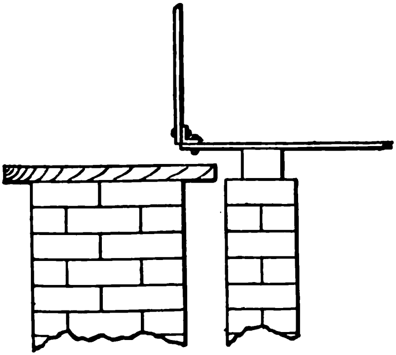

Fig. 15.

When this occurs in a salt-pan the calcium carbonate (which is almost always accompanied by oxide of iron) deposits on the top of the fire plates, and forms what is technically called 'sand scale.' This has to be broken from time to time with a blunt pick and fished out of the pan, otherwise the plates would get red hot and burn away. When a pan begins to leak, the brine often crystallises as it drops into the flue, and forms a stalactitic mass, which is locally called a 'cat.' This is not the only trouble caused by a leaky pan, for, in addition, hydrochloric acid is frequently formed, through the decomposition of sodium chloride by sulphur dioxide in the presence of water. The sulphur dioxide is generated by the combustion of small quantities of pyrites in the fuel. All British salt works are now under Government inspection, and the chimney gases are tested from time to time by the inspectors.

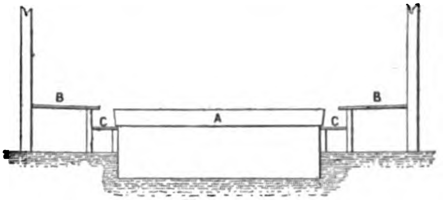

Fig. 16.

A. Salt-pan. B, B. The hurdles. C. Standing aside.

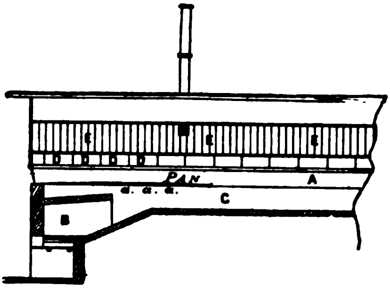

Fig. 17.—Longitudinal Section of a French Salt-pan, showing Shape of Pan and Arrangement of Wooden Cover.

A. Salt-pan. *a, a, a.* Raised fire-plates. B. Fireplace. C. Flue. D, D, D, &c. Movable doors in cover. E, E, E. Cover forming hurdles.

If brine contains calcium sulphate, it deposits it when heated. This falls to the bottom of the pan, and forms a scale which frequently contains a large quantity of salt. It sometimes accumulates to a thickness of 4 ins. and is known as 'pan scale.' On account of the growth of scale and the consequent decreased

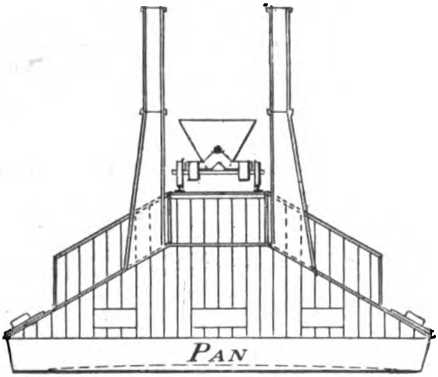

Fig. 18.—Front view of a French Salt-pan, showing Chimneys to carry off the Steam.

Dotted line shows curve of the pan over the fires.

efficiency of the pan, it becomes necessary after working for a given time to run off all the liquid from the pan and remove the scale. This operation is termed 'picking' the pan.

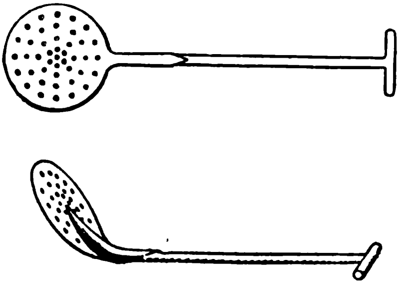

Fig. 19.

Solar salt. In some places, where the natural brine is so weak or fuel is so scarce that evaporation by artificial heat is not remunerative, salt is made by exposing the brine to the rays of the sun in large wooden pans resting on the ground. Such pans are frequently provided with movable covers which are pushed aside in fine weather and drawn over if rain comes.

Along the sea-coast of countries which possess a dry climate or habitually experience a hot summer, salt is made by solar evaporation of sea water.

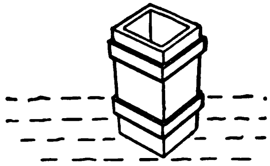

Fig. 20.—A Box for Lump Salt.

A large piece of land, slightly below high-water mark, is levelled and surrounded by a wall or bank. The ground is, if necessary, puddled with clay to make it water-tight, and the enclosed space is divided into compartments by internal walls. Sea water is admitted at high tide, and, after being allowed to deposit any solid matter it may contain, is run from compartment to compartment until salt crystallises out. This is then raked together into heaps and allowed to stand while the more deliquescent salts, such as magnesium chloride, run away.

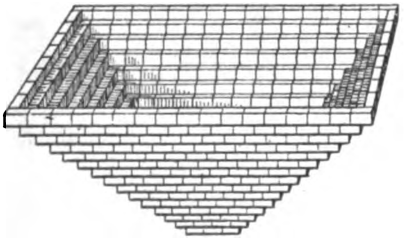

Fig. 21.

These salt gardens (German, *Salz-Gärten*) are freely worked in Portugal, Spain, France, Austria, Corsica, Italy, Cyprus, Smyrna, and in India, and produce very large quantities of salt. The product is naturally much more impure than that made from brine derived from rock salt.

The mother-liquors are comparatively rich in bromides of calcium and magnesium, and are sometimes employed for the extraction of bromine.

In some cold countries, such as Russia and Sweden, salt water is allowed to freeze, and the ice, which consists of nearly pure water, is removed. By repeating this several times, a mother-liquor is obtained which is sufficiently strong to boil down. The salt obtained does not contain more than 75–85 p.c. of sodium chloride.

J. I. W.

Sodium bromide can be prepared by neutralising a solution of sodium hydroxide or carbonate with hydrobromic acid, but is usually made technically by adding bromine to a hot solution of caustic soda, mixed with powdered charcoal. Sodium bromide and bromate are first produced, but on evaporating the solution to dryness and heating the residue, the latter is reduced by the charcoal.

$$6NaOH+3Br_2=5NaBr+NaBrO_3+3H_2O$$
$$2NaBrO_3+3C=2NaBr+3CO_2.$$

Sodium bromide forms white crystals which, when produced from solutions below 50°, contain two molecules of water and belong to the monoclinic system. Above that temperature the anhydrous salt, crystallising in cubes of sp.gr. 3·014, is obtained. A second hydrate, $NaBr,5H_2O$, separates out from strongly cooled solutions of the salt. The anhydrous salt melts at about 760°; it dissolves in water with considerable absorption of heat, its solubility being given below (De Coppet, Ann. Chim. Phys. 1883, [vi.] 30, 420):—

Temp.	—10°	0°	20°	40°	60°	80°	100°	120°
Grams NaBr in 100 gms. water	75·1	79·5	90·3	105·8	117	118·5	120·5	122·5

The saturated solution boils at 121° It is also soluble in alcohol and in acetone, one part of the salt requiring at the ordinary temperature 14 parts of ethyl alcohol or 4·6 parts of methyl alcohol for solution. For the sp.gr. of sodium bromide solutions, *see* Kremers (Pogg. Ann. 1855, 96, 39); for their electrical conductivity, *see* Ostwald (Allgem. Ch., Leipzig, 1893), and for their refractive indices *see* Borgesius (Wied. Annalen, 1895, 54, 233).

Sodium bromide is occasionally employed in medicine in place of the potassium salt, which it resembles in its physiological effects.

Sodium iodide. This salt can be prepared artificially in a manner analogous to that given under sodium bromide (*q.v.*), or by double decomposition between solutions of ferrous iodide (prepared by acting on iron filings with iodine in the presence of water) and caustic soda. It separates from solutions at temperatures under 65° in white, slightly deliquescent crystals containing two molecules of water, which are isomorphous with the corresponding hydrates of sodium bromide and chloride. Above 65° the anhydrous salt is obtained. Panfiloff (J. Russ. Phys. Chem. Soc. 25, 272) has obtained the hydrate $NaI,5H_2O$ by cooling a solution of the salt to —14°. Sodium iodide melts at about 650°. The sp.gr. of the anhydrous salt is 3·665. The salt is very soluble in water, 100 parts of this liquid dissolving at

0°	10°	20°	30°	40°	50°	60°	80°	100°
159	169	179	190	205	228	257	295	302

parts of sodium iodide (De Coppet, Ann. Chim.

Phys. 1883, 30, 420). The boiling-point of the saturated solution is 141°. One part of the salt dissolves in 1·7 parts of ethyl or 1·2 parts of methyl alcohol at ordinary temperatures, and it is also very soluble in acetone. If sodium iodide be kept fused for a considerable time in contact with air, it loses a little iodine. Heated with carbon in presence of air it is almost completely converted into carbonate. For the electrical conductivity of sodium iodide solutions, *see* Kohlrausch and Holborn, Leitvermögen der Elektrolyte, Leipzig, 1898. For the melting-points of mixture of KI and NaI, *see* Kurnakow and Shemtschushni, Chem. Zentr. 1906, i. 527. A compound $NaI_8,2(C_6H_5NO_2)$ has been isolated by Dawson and Goodson (Chem. Soc. Trans. 1904, 85, 796) from a solution of sodium iodide in nitrobenzene saturated with iodine, in the form of greenish metallic crystals which deliquesce in the air. Sodium iodide, like sodium bromide, is used to a small extent in medicine in place of the potassium salt. See also vol. iii. p. 153.

Sodium hyposulphite, *see* under *Hyposulphurous acid*, art. SULPHUR.

Sodium sulphides. *See* p. 29.

Sodium sulphites. Three sulphites of sodium are known, *i.e.* the normal sulphite, the bisulphite, and the metabisulphite.

Normal sodium sulphite can be prepared in the anhydrous state by heating sodium bisulphite with the theoretical amount of sodium bicarbonate or by passing ammonia gas into a solution of sodium chloride and ammonium sulphite. If a cold, saturated solution of the heptahydrated salt be heated, a crystalline precipitate of the anhydrous salt is formed.

The salt is unalterable in air and dissolves readily in water; by evaporation of the solution white, monoclinic crystals of the heptahydrate are obtained. These have a sharp taste, effloresce on exposure to air, and dissolve fairly easily in water, yielding a solution which reacts alkaline. The solubility for different temperatures has been determined by Kremers—

Temperature	0°	20°	40°	100°
Grams Na_2SO_3 per 100 of water	14	29	50	33

According to Mitscherlich (Pogg. Ann. 1827, 12, 140) the solubility of the salt reaches a maximum at 33°, which temperature represents the transition-point of the hydrated into the anhydrous salt.

Dilute solutions of sodium sulphite oxidise rapidly, but a 20 p.c. solution is stable (Lumière and Seyewetz, Revue gén. chim. pur. et app. 1896, 7, 111). The oxidation is greatly accelerated by the presence of small quantities of copper sulphate, whilst potassium thiocyanate and mannitol have a retarding action. On heating in air sodium sulphite yields a mixture of sulphide and sulphate—

$$4Na_2SO_3=3Na_2SO_4+Na_2S.$$

On the large scale sodium sulphite is prepared by passing sulphur dioxide through a solution of sodium carbonate or through a vessel filled with the crystallised salt, until the product has an acid reaction. The resulting solution, consisting chiefly of bisulphite, is converted into the normal sulphite by adding sodium carbonate to the boiling solution until no more carbon dioxide is evolved. The liquid is then allowed to settle, decanted and evaporated to the crystallising-point.

(i.) $Na_2CO_3+2SO_2+H_2O=2NaHSO_3+CO_2$.
(ii.) $2NaHSO_3+Na_2CO_3=2Na_2SO_3+CO_2$.

Sodium bisulphite $NaHSO_3$ is produced by saturating a solution of sodium carbonate with sulphur dioxide. It forms a white powder, smelling of sulphur dioxide, is only sparingly soluble in water, and is precipitated from its aqueous solution by alcohol. On heating, it decomposes, evolving sulphur and sulphur dioxide and leaving a residue of sulphate. A crystallised trihydrate and tetrahydrate have been obtained by strongly cooling the solution of the bisulphite made in the above mentioned way; both are very unstable, and rapidly change into the stable metabisulphite.

Sodium metabisulphite $Na_2S_2O_5$ is prepared by supersaturating a solution of sodium carbonate with sulphur dioxide, when it is obtained in anhydrous crystals on cooling the solution. The salt only slowly oxidises on exposure to air at the ordinary temperature; on cautious heating at 80° it loses 1 molecule of SO_2, and on further rapid heating evolves sulphur and sulphur dioxide, leaving sodium sulphate

$$2Na_2S_2O_5=2Na_2SO_4+SO_2+S$$

(Schultz-Sellack, J. pr. Chem. [i.] 110, 459).

It is made technically by the method described above or by passing sulphur dioxide over monohydrated sodium carbonate (Carey and Hurter, Eng. Pat. 4512, 1882).

The normal, bi-, and metabisulphites of sodium are largely employed in various industries, chiefly as antiseptics, reducing agents, and sources of sulphur dioxide. The boiling solution of the sulphite has the property of readily dissolving the resin, gum, &c., contained in wood without in any way affecting the cellulose. Hence the bisulphite is used in preparing the 'sulphite pulp' now so largely made from wood for use in the manufacture of paper. It is also employed in the calico-printing and colour industries as a reducing agent, and as an 'antichlor' for removing the last traces of chlorine from the bleached pulp obtained in paper-making. It also finds application as an antiseptic for steeping grain, preserving food, &c., and a strong solution is employed as a sterilising medium for brewers' casks. Owing to its property of combining with many organic aldehydes and ketones to form crystalline, mostly insoluble, additive compounds which can easily be isolated and purified, it is used in the laboratory in the identification and purification of these classes of compounds. Normal sodium sulphite finds application in medicine as an antiseptic and as an antizymotic for internal use. Its solution has been proposed for use in gas analysis, owing to its power of absorbing nitric oxide. Both the normal and metabisulphites are extensively employed in the preparation of photographic developers for preventing the oxidation of the pyrogallol, hydroquinone, &c., which these contain, and the normal salt has been proposed by Abney (Phot. News, 1885, 370) as a substitute for the sodium thiosulphate used to dissolve out the unaltered silver salts in the process of fixing photographic prints. A large number of double sulphites of sodium with other metals are known, the most interesting being the sodium potassium sulphite, which was formerly thought to exist in two isomeric forms. This view has, however, been shown to be incorrect (Barth, Zeitsch. physikal. Chem. 1892, 9, 176; Arbusoff, J. Russ. Phys. Chem. Soc. 1909, 41, 447).

Sodium thiosulphate. See p. 29.

Sodium silicates. The solubility of silica in alkalis was well known to the alchemists, a method for preparing sodium silicate being described as early as 1520. They were also well acquainted with many of the properties of the resulting solution, such as the coagulation which takes place on adding an acid. Sodium silicates are prepared by fusing together silica and sodium carbonate or by digesting finely-divided silica with caustic soda solution. The composition of the resulting silicate varies with the duration of the heating, the temperature, and the relative amounts of silica and alkali employed. A number of sodium silicates have been prepared and examined by Ordway (Amer. J. Sci. [ii.] 32, 162, 337; 33, 27, 35; 35, 35, 185), but the metasilicate Na_2SiO_3 is the only well-defined one. It may be obtained pure by digesting the theoretical amount of freshly-precipitated, hydrated silica with caustic soda solution. On adding twice the volume of alcohol it is precipitated as a white, crystalline powder. Only the metasilicate has been obtained in the crystalline condition, the others forming amorphous, glassy bodies.

Pure sodium metasilicate is a white, crystalline salt, melting at about 1000° (Kultascheff, Zeitsch. anorg. Chem. 1903, 35, 187). Hydrates containing 5, 6, 7, 8, and 9 mols. of water have been described, but their existence is somewhat doubtful. The aqueous solution of the salt has an alkaline reaction owing to hydrolytic dissociation. Kahlenberg and Lincoln (J. Phys. Chem. 1898, 2, 81) state that at a dilution of 1 grm. mol. in 48 litres the hydrolysis is complete, according to the equation:

$$Na_2SiO_3+H_2O=SiO_2+2NaOH$$

the silica being in colloidal solution.

Aqueous solutions, even dilute ones, of sodium silicate are precipitated by alcohol. On treatment with acids, even carbonic acid, the salt is completely decomposed with separation of gelatinous silica; the alkaline carbonates and chlorides, especially ammonium chloride, also precipitate the silica. Salts of the alkaline earths give precipitates of insoluble double silicates. Commercial sodium silicate, also called soluble glass or water-glass, usually approximates to the composition $Na_2O,4SiO_2$, containing about 79 p.c. of silica. It is prepared on the large scale by two processes, known as the dry and wet methods respectively. In the dry method, a mixture of powdered quartz or white sand and either sodium carbonate or sulphate is fused in a Siemen's regenerative furnace or similar gas-fired furnace for 5–8 hours at a temperature of about 1100°. Continuous coal-fired furnaces are also in use, which are capable of turning out 1250 kilos. of water-glass in 24 hours with a consumption of 1500 kilos. of coal.

The product is run out in a fused condition into an iron receptacle and allowed to cool. Typical mixtures employed for the charge are given below, the coal being added to assist in the reduction of the carbonate or sulphate.

1	2
100 lbs. powdered quartz	100 lbs. powdered quartz
28 lbs. calcined sodium carbonate	60 lbs. calcined sodium sulphate
	15–20 lbs. coal
3	4
180 lbs. white sand	180 lbs. white sand
110 lbs. sodium sulphate	100 lbs. 50 p.c. sodium carbonate
10 lbs. coal	3 lbs. coal

The fused product is broken up by a stone-breaker or ground by suitable machinery and dissolved by long boiling with water, preferably under pressure. The resulting solution is allowed to clarify, and is then evaporated to 40°Bé. in iron pans. The small proportion of sulphide sometimes present from the reduction of the sulphate can be removed by adding a little copper scale or litharge when preparing the solution. 100 lbs. of the solid yield about 300 lbs. of a solution of 40°Bé.

The wet method of preparation is largely employed on account of the greater uniformity of the product, and the fact that it is obtained at once in the form of a solution. It consists in digesting silica—preferably infusorial earth—with a solution of caustic soda of sp.gr. 1·22–1·24 (prepared by causticising a solution of sodium carbonate with lime) under three or four atmospheres pressure. The liquid is heated by blowing in steam and is kept stirred by machinery. Complete solution is attained in about 3 hours, as shown by withdrawing a sample, when the suspended matter ought to settle rapidly and be of a brick-red colour (Fe_2O_3), whilst the liquid should be almost free from alkaline reaction. The caustic soda must not be above 1·24 sp.gr. as a stronger solution holds the fine sand and ferric oxide in suspension for a long time, such solutions not clarifying properly even after standing for several days. The clarified liquid is drawn off and concentrated to the required strength (usually 1·7 sp.gr.) in iron pans. 2·8 parts of infusorial earth are employed for every part of caustic soda, and the resulting water-glass solution has a density of about 1·18, the decrease in specific gravity being due to the dilution produced by the condensed steam. Instead of infusorial earth, other forms of silica, such as powdered flints, quartz, &c., can be employed, but the digestion must then be continued for a longer time and under 7–8 atmospheres pressure.

A pure silicate may be made from the crude product by passing a current of carbon dioxide through the solution, filtering off the precipitated hydrated silica and redissolving it in caustic soda.

The aqueous solution of sp.gr. 1·7 usually has the following composition: silica 32–33 p.c., soda 16–16½ p.c., other sodium salts 2½–3 p.c., water 48–49 p.c.

A water-glass known as ‘double soluble glass’ and containing about equal proportions of sodium and potassium silicates, is prepared by using the proper quantities of potassium and sodium carbonates in place of sodium carbonate alone. It is said to give a thinner solution than either the potassium or sodium salt of corresponding strength.

Commercial water glass is sometimes colourless, but usually has a brownish or greenish colour. It is nearly insoluble in cold water, but dissolves completely, although slowly, in boiling water, the solubility decreasing as the percentage of silica in the substance increases. Silicates containing more alkali than corresponds with the composition $Na_2O{\cdot}2\frac{1}{2}SiO_2$ are deliquescent, and too poor in silica to be applicable to the ordinary uses of water-glass (Ordway, Amer. J. Sci. [ii.] 35, 193).

The following is a list of patents dealing with the manufacture of water-glass :—

Ransome, Eng. Pats. 10360, 1844; 10665, 1845; 1666, 1853; 645, 1855; 2267, 1856. Kuhlmann, Eng. Pat. 367, 1853. Losh, Eng. Pat. 14208, 1852. Gossage, Eng. Pats. 762, 1854; 799, 1099, 1859. Kayser, Williams, and Young, Eng. Pat. 11493, 1887. Sievert, Eng. Pat. 4021, 1890. Crosfield and Markel, Eng. Pat. 18998, 1894. Garroway, Eng. Pat. 2489, 1896. I. J. Brown, Eng. Pat. 24237, 1902. Watson, Eng. Pat. 25394, 1904.

Sodium silicate is largely used on account of its detergent properties as an addition to soap, principally to those intended for toilet use, as it imparts hardness and durability. Two typical analyses of such soaps are given below :—

	I.	II.
Soda . .	12 p.c.	12·5 p.c.
Silica . .	10 „	8·5 „
Water . .	30 „	33·0 „
Fatty acids .	48 „	46·0 „

Water-glass is also employed in the calico-printing and dyeing industries as a fixing agent for pigments; in printing indigo; as a resist for certain colours, and in the finishing of cotton goods. It is a constituent of certain lead-free enamels for glazing pans, &c., intended for domestic use, and is occasionally employed in the basic linings of Bessemer converters. It is used in fixing fresco-painting (stereochromy), for rendering wood, paper, &c., uninflammable, in bleaching jute, for preventing wood from rotting, and for preserving eggs. A mixture of 2 parts fluorspar and 1 part powdered glass made into a thick paste with water-glass is used as a cement for glass and porcelain. The so-called 'artificial vegetation' is made by dropping small fragments of cobalt chloride, ferrous sulphate, and many other salts into a solution of sodium silicate, when frond-like appearances, due to the formation of insoluble metallic silicates, are producd.

Sodium silicate is largely used for impregnating sandstone and other porous stones as a protection against weathering. The stone is treated with a solution of water-glass, followed by the application of a solution of calcium chloride or aluminium sulphate, which causes the deposition of an insoluble silicate in the pores of the stone, greatly increasing its hardness and durability. The soluble sodium salt formed is removed by a subsequent washing (*see* also Burnell, J. Soc. Arts, 8, 240). An important application of water-glass is in the manufacture of artificial stone. The following is an outline of the process used at an English works for the manufacture of chimney-pots, mouldings, &c. The sand or sandstone employed having been ground wet and passed through a 40-mesh sieve is thoroughly dried and mixed in a revolving pan provided with scrapers and edge mixers with sufficient liquid water-glass to form a moist, coherent mass. It is then pressed into moulds and is saturated before removal with a solution of calcium chloride (prepared by running hydrochloric acid over calcspar) drawn through by a vacuum equal to about 20 ins. of mercury. Calcium silicate having thus been formed as above, the stones are transferred to boiling tanks heated by steam, and, after a sufficient time to complete the setting, are conveyed to washing tanks, in which they are subjected to the action of running water for a fortnight, to remove the whole of the sodium chloride.

Sodium sulphate, technically called 'sulphate,' or 'salt-cake,' was first obtained by its discoverer, Glauber, as described by him in 1658, exactly in the same way as it is prepared now, by the decomposition of common salt by sulphuric acid. The crystallised salt, containing 10 molecules of water of hydration, is still called 'Glauber's salts.' Both the anhydrous and the hydrated salts are found in many places in nature; the former, as a mineral, is called *thenardite*, the latter *mirabilite*. Large quantities of sodium sulphate occur native, especially in Spain, at Lodosa, in the Ebro valley, and elsewhere, and in the Western States of North America.

The double sodium and calcium sulphate called *glauberite*, also occurs naturally in large quantities and in many places.

Sodium sulphate is frequently obtained as a *by-product* of other manufactures, of which we mention only two.

Impure sodium sulphate is obtained in the (now almost obsolete) manufacture of hydrochloric acid in cast-iron cylinders from common salt and sulphuric acid; this product, called *cylinder-cake*, mostly contains from 7 to 10 p.c. of undecomposed sodium chloride. On the other hand, the *nitre-cake*, obtained in decomposing sodium nitrate by sulphuric acid, always contains a considerable proportion of acid sodium sulphate $NaHSO_4$.

A certain quantity of sodium sulphate, principally in the state of Glauber's salts, is made from the residues left on dissolving the crude carnallite ('Abraumsalz') at Stassfurt. The latter contains a large quantity of insoluble *kieserite* $MgSO_4,H_2O$, which, on being exposed to the weather, or brought into contact with water for some time, gradually yields soluble magnesium sulphate $MgSO_4,7H_2O$. The residues at the same time contain much common salt, and, if necessary, more of the latter is added, so as to bring up the quantity to the proportion of 2 NaCl to 1 $MgSO_4$. When this mixture is dissolved in water and the solution is exposed to a natural or artificial cooling a few degrees below 0°, the following decomposition (noticed by Scheele as early as 1787) sets in :—

$$MgSO_4+2NaCl=Na_2SO_4+MgCl_2.$$

The sodium sulphate crystallises as Glauber's salts, the magnesium chloride remaining behind. Many thousands of tons of Glauber's salts are made at Stassfurt in this way.

By *heating metallic sulphides with common salt in the presence of air*, sodium sulphate is produced in considerable quantities. This process has been known for more than a century in metallurgy, where it is employed for extracting silver and copper from their ores. In this case, of course, the metal is the product really aimed at, and the sodium sulphate is in actual practice run to waste in the shape of impure solutions. In 1842 Longmaid introduced a modification of this process, by which the sodium sulphate was obtained in a marketable form; but this was only practicable when employing ordinary iron pyrites, free from copper, and the sodium sulphate obtained in this way could not compete with that made in the usual way from common salt and sulphuric acid, as found out in the working of Longmaid's process in several places through a number of years. A similar process is employed up to this day for the recovery of copper from cupreous pyrites; but here the sodium sulphate is lost, all attempts to recover it having failed on account of expense.

Iron pyrites is, however, employed in a different manner for manufacturing nearly all the sodium sulphate found in trade—namely, either by first manufacturing sulphuric acid and employing this for decomposing common salt, or by the direct process of Hargreaves and Robinson, in which the pyrites-kiln gases are made to act upon common salt under such circumstances that sodium sulphate and hydrochloric acid are produced. We shall now describe these two processes.

The *decomposition of sodium chloride by sulphuric acid* is the process employed by Glauber, and by Leblanc, and at present produces by far the larger part of the sodium sulphate used. We shall omit mention of the obsolete processes of performing this operation in glass retorts or iron cylinders, and describe the process as now carried out.

The raw materials for the salt-cake process are:

1. *Common salt*—that is, impure sodium chloride. In England 'pan-salt' is generally used, the porous condition and coarse grain of which is of great advantage in the process; it is also generally fairly pure, but contains varying quantities (8 to 10 p.c.) of water. Rock salt is also employed to a great extent; this must be coarsely crushed, not finely ground, and should be as free as possible from calcium sulphate. As is to be expected, the impurities and their amounts permissible in salt to be used for the production of salt-cake depend on the purpose for which the salt-cake is afterwards to be used.

2. *Nitre-cake*—that is, the residue from the manufacture of nitric acid, consisting of a mixture of a normal and acid sodium sulphate. Nitre-cake is frequently mixed off with an ordinary charge of salt. The free acid determined by analysis replaces part of the sulphuric acid which would otherwise be required to decompose the salt used. The nitre-cake is broken into lumps which readily melt in the decomposing pan.

3. *Sulphuric acid.* This should be neither too weak nor too strong, preferably about 140°—that is, at the strength it usually comes from the Glover tower. Stronger acid acts too rapidly, and yields badly mixed batches; weaker acid retards the operation and injures the pots.

The decomposition of NaCl by H_2SO_4, though commencing at ordinary temperature, is not completed until a dull red heat is attained. It is the usual practice, therefore, to divide the operation into two stages, the first of which is performed almost always in a cast-iron pot, the second in a brick furnace.

The two stages are generally expressed as:

1. $H_2SO_4+2NaCl=NaHSO_4+NaCl+HCl$
2. $NaHSO_4+NaCl=Na_2SO_4+HCl$.

In practice more than 50 p.c. of the reaction takes place in the first stage. The actual amount depends on the temperature of the charge in the decomposing pan or pot, and varies from 65 to 75 p.c. of the whole.

The *salt-cake pots* are now always made in the shape of shallow cast-iron dishes, 9 to 11 ft. in diameter, and 1 ft. 9 ins. to 2 ft. 6 ins. deep; the thickness of the metal varies from 5 to 7 ins. in the centre, and from 2 to 3 ins. at the sides. These 'pots' weigh from 5 to 6½ tons, and must be made of a special mixture, so as to combine resistance to chemical action with toughness and resistance to changes of temperature. Their edge is sometimes quite plain, sometimes provided with an ordinary horizontal flange; but, best of all, with an upstanding margin on a horizontal flange as shown in Fig. 22 (*v.* p. 23). In the latter case they are arched over in such a way that the arch is sprung from the pan-edge itself, so that any leak occurring here cannot cause the escape of hydrochloric acid into the fire-flues. The arch or dome over the pot is built of acid-resisting brick, usually set in a mixture of salt and mortar. The common custom is to fill the pot with salt and then heap on more salt until a conical mound of salt is obtained of the desired shape, and the arch is then built, using the mound of salt as the centering.

Near the decomposing-pan there must be a cistern for measuring the sulphuric acid to be run in for each charge. It is preferable that this acid should be moderately warm, and this can be attained by employing as gauge-vessel an iron pan lined with lead, and placing this over a hot flue.

The sulphuric acid from the gauge-vessel is run into the pan through a luted lead pipe which passes through the dome or arch and delivers a slow stream of acid on to the salt in the centre of the pan.

The *calcining-furnace* (*roaster or drier*) may be of various patterns—either a reverberatory (*open*) furnace, or a muffle-furnace (*close* or *blind* roaster). The open-furnaces have now nearly all disappeared and been replaced by muffle-furnaces owing to the greater difficulties and expense of efficiently cooling and condensing the hydrochloric acid produced in the roaster when mixed with the products of combustion from the fireplace; on the other hand, the muffle- or closed-furnaces are naturally more difficult to construct and cost more in repairs.

Figs. 22 and 23 show a common form of open-furnace with the pan attached in sectional elevation and plan. *a* is the fireplace of the furnace, the area of which is comparatively small compared with that of the furnace-bed; *b* is the furnace-bed, with two working doors *f*; *c*, the outlet for the mixed fire-gas and acid-gas; *d*, the decomposing pan, covered by an arch resting upon the pan-flange; *e*, the gas-pipe;

h, a balanced double cast-iron damper, which closes the passage *k* (Fig. 23) (the 'shoving hole') between pan and furnace; *m*, the fire-grate of the pan, covered by the arch *n*, pierced by a number of holes; *o o*, a circular wall on which the pan is supported, equally pierced with holes, so that the flame escapes into the annular space outside, and thence into the main flue. It is evident how the setting of the pan aims at causing the flame to avoid striking the pan, and to distribute the heat as equally as possible.

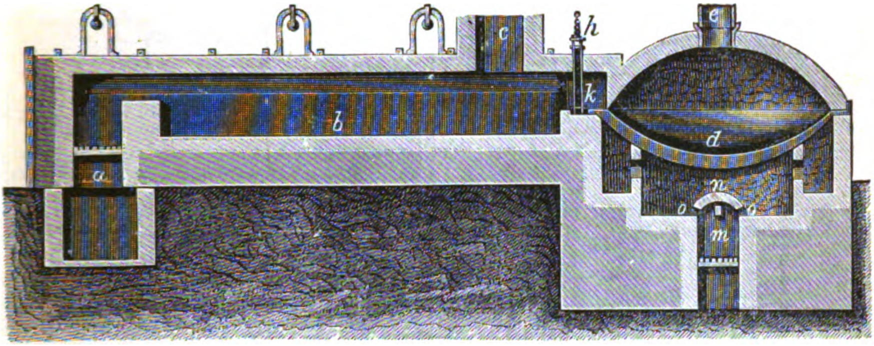

FIG. 22.

In the early days of the muffle salt-cake furnaces very considerable difficulties were experienced in keeping the furnace sufficiently arch tight to prevent leakage of the HCl from inside the muffle into the chimney flue. This was not only a source of loss of HCl, but was liable at any time to cause an infringement of the Alkali Acts which specify in Great Britain a maximum HCl content of the chimney gases of 0·2 grn. HCl per cubic foot.

To meet this difficulty suggestions were made by Muspratt and by Gamble of means to place the flue gases under a higher pressure than the gases inside the muffle and thus to cause any leakage which might take place to be from the fire-gas flue into the muffle. In 1876 Deacon brought out the 'plus pressure' salt-cake furnace which bears his name, and which is to-day by far the most extensively used of all the hand salt-cake furnaces (Figs. 24–27).

The plan adopted by Deacon was extremely simple, and consisted in the building of the fire-place on a lower level than the furnace, thus utilising the pressure due to the ascending current of hot gases to balance the pull of the chimney in the flue space over the furnace arch.

Figs. 24 and 27 show how the flame generated on a grate far below the top of the muffle is made to play, first on the top, then under the bottom, of the muffle, which is supported by a number of dwarf walls. The flame then travels on by an exit flue under the bottom of the pan, which is thus heated without any expenditure of special fuel.

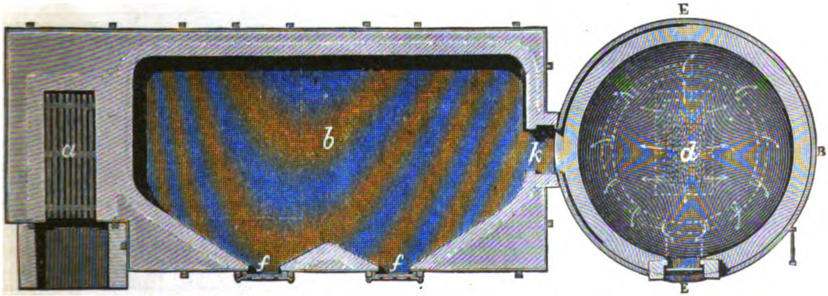

FIG. 23.

It will be noticed in both the illustrations of the open-furnace and the Deacon-furnaces, Figs. 22 and 23, that great care is taken in the setting of the pan so as to ensure, as far as possible, equal heating over its surface. This care is essential to the life of the pan which depends on the mixture of iron used in the casting, on the strength of the vitriol used, on the design of the pan setting, and, of course, also on the carefulness of the men working the charges. With attention to these points salt-cake-pans will last while the furnaces produce up to 4000 tons of salt-cake.

Whether the roaster be an open or a blind one, the work in salt-cake making, as far as the pan is concerned, is almost entirely the same. Only the size of the batches differs in the two cases. With open roasters, which admit of finishing a batch once an hour, or even oftener, batches are made of 6 or 8, or at most 10, cwt. of salt. With close roasters, requiring 2 hours for each batch, they are in England made larger, up to 18 cwts. of salt; but on the Continent even then smaller batches are preferred. In any case, the pan, after removing the last batch, is carefully cleaned from crusts, which would burn fast and cause it to crack prematurely. A small quantity of the next charge of salt is then thrown into the pan, and the sulphuric acid, preferably heated to some extent, is started running in; the rest of the salt is then thrown in as quickly as possible. The quantity of the acid must, of course, be exactly regulated, and in measuring it in the gauge-vessel (*cf.* p. 22), not merely the volume and the hydrometric strength, but also the temperature of the acid must be carefully observed, since the specific gravity by itself is no index of the strength of acid, without taking into account the temperature. A table for reducing the specific gravities of sulphuric acid of various strengths to any other temperature between 0° and 100°C. is given in The Technical Chemist's Handbook, by Lunge.

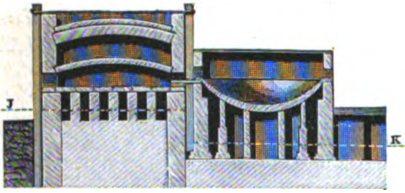

FIG. 24.

As the Twaddel hydrometer is practically universally employed in England, it is useful to remember that for sulphuric acid of the strength here used, 10°F. in temperature corresponds to a rise or fall of 1°Tw. in specific gravity.

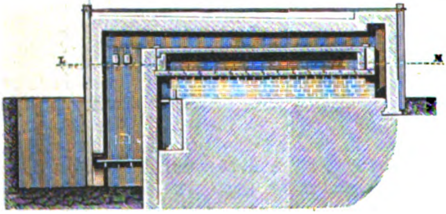

FIG. 25.

Theoretically, 100 parts of pure sodium chloride would require 83·82 parts of pure monohydrated sulphuric acid, or 106·28 parts of acid at 144°Tw., measured at 15°C. But common salt is never pure NaCl. This must be taken into account as well, by daily testing the salt at least for moisture, and allowing, say, 2 p.c. for other impurities. Thus, 100 parts of salt containing 95 p.c. of NaCl would take 79·63 parts of SO_4H_2 or 100·97 parts by weight of sulphuric acid of 144°Tw., measured at 15°C. This means 100·97/1·72=58·70 litres of acid of 144°Tw. for each 100 kilos. of 95 p.c. salt, if the acid be measured at 15°C.; but, if the temperature were 100°C., the rates of the specific gravities (as per the table quoted above) is as 1·64 and 1·72, and hence the 58·70 litres will become 61·56 litres, or, directly calculated, 100·97/11·64=61·56 litres.

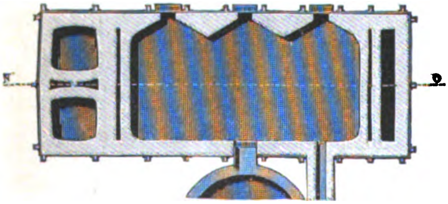

FIG. 26.

Practically a little more acid must be employed, partly because the mixture can never be theoretically perfect, partly because a little sulphuric acid or anhydride is volatilised, especially in the roaster. With open roasters the excess of vitriol required is about 5 p.c.; with close roasters, only 2 or 3 p.c. Whether the proportions employed have been correct or not must be decided in each particular case by testing the salt-cake, which ought not to contain more than 0·5 p.c. undecomposed salt, or above 1 p.c. free acid (calculated as SO_3).

The first reaction between the ingredients in the salt-cake pot is very violent, and there is a tendency of the mass to rise and to froth over, which is counteracted by throwing in a little tallow. The salt should be dissolved in the vitriol, which is easily done with common pan-salt, but much less easily with rock salt, and is assisted by occasional stirring, the handle of the rake passing through a hole in the charging door. The fire is then increased to drive off more hydrochloric acid, but not too much, lest the batch becomes too stiff; the work is regulated in such manner that the batch is ready to be 'cast' or 'shoved' into the roaster, just when the last charge has been drawn from the latter. For this purpose the damper *h* (Fig. 22) is raised. The work in the roaster must be carried on in such manner that the batch is thoroughly turned over and mixed.

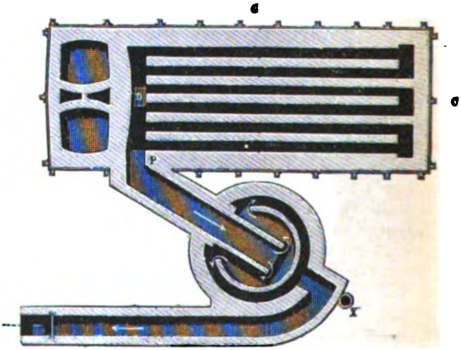

FIG. 27

The temperature within the furnace should ultimately be a red heat, and no more vapours should be seen rising from the mass. Still, it usually happens that, on drawing the batch out of the furnace, gases are given off (those of sulphuric anhydride being less pungent than those of hydrogen chloride), and, to avoid nuisance, the mass is frequently first drawn into a closed box, where it cools down and is then removed without causing inconvenience.

The yield of salt-cake is very nearly that calculated by theory from the dry salt. It may be taken as about 120 parts upon 100 of dry salt. Calculated upon the sulphur burnt in the pyrites kilns, it varies from 405 to 430 parts to 100 of sulphur actually burnt, open furnaces yielding rather less than close ones (owing to the volatilisation of SO_3).

The consumption of fuel varies in hand-furnaces from 30 to 50 parts to 100 of salt-cake; it is higher with close roasters than with open ones, but the difference is less where the pans are heated by the waste fire of the muffle-furnace.

Mechanical salt-cake furnaces have been constructed by many inventors to economise labour and coals. We mention among such furnaces those of Jones and Walsh (1875; improved in 1887; *cf.* Chem. News, 35, 51); Black and Hill (1877); Cammack and Walker (1876); Black and Larkin (1884); Thomson and Worsley (Eng. Pats. 21945 and 21946, 1894). Some of these have not answered in the long run, and we shall confine ourselves to a description of one of the most successful of mechanical salt-cake furnaces, that of Mactear (1879, described and discussed J. Soc. Chem. Ind. first General Meeting, 1881, p. 29 *et seq.*), and shown in Fig. 28. It consists of a revolving circular bed, covered by a fixed arch, the fire passing between them, and the access of air being prevented by a 'lute' filled with salt-cake. In the centre there is a kind of pot into which both salt and acid are continuously fed, and in which they are mixed. The pasty mass overflows into the outer beds, and is both continually stirred and gradually carried to the outer circumference by means of a number of stirrers, which are protected against the action of the fire and the acid gases by being placed between the gas-flues. The finished salt-cake, arriving at the outer edge, falls into the delivery trough running all round the furnace, and at the same time forming the 'lute.' The acid vapours and products of combustion pass away together in two flues, arranged at each side of the row of stirrers. The bed of the furnace is lined with fire-brick, boiled in tar and set in a special cement, which becomes even harder when subjected to the action of the heat and sulphate.

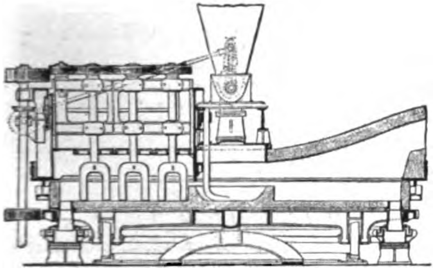

FIG. 28.

A great point in the Mactear furnace is the continuous decomposition of salt. Thus a continuous and even stream of hydrochloric acid is evolved, and, although this is mixed with all the fire-gases, it was claimed that the condensing-plant required is decidedly less than that found necessary with close furnaces. This, however, is not in agreement with modern practice, and makes no allowance for the much more extensive and expensive cooling plant necessary to cool the gases when mixed with the products of combustion as they are with the Mactear furnace than in the case of a muffle-furnace, such as the Deacon 'plus pressure' salt-cake furnace.

The Mactear furnace was first fired with coke; then 'Wilson' producers were attached to it (compare above); but these have had to be given up again for coke, so that the hoped-for economy in firing has not been realised

The Black and Larkin furnace, which is combined with an ordinary pan, is a peculiarly constructed muffle, heated from without by a number of small fires, both above and below, practically on the 'plus-pressure' system, with a very efficient mechanical stirring apparatus, thus permitting all the work to be done with closed doors, and avoiding 'low-level escapes.' Naturally the condensation of the hydrochloric acid is as easy in this case as with ordinary close roasters. One such furnace decomposes from 72 to 80 tons of salt per week. These furnaces have been successful, and are still at work in the place where they were originally introduced. Another mechanical furnace, composed of two revolving cylinders, is that of A. Walker (Eng. Pat. 9760, 1887). Generally speaking, although mechanical salt-cake furnaces have been used for so many years and have absorbed so much skill and patience in their design, they have not been generally adopted, owing to the fact that their undoubted economy in labour and power of producing a more uniform salt-cake is more than balanced by the higher first cost, cost of repairs, and the difficulties of condensation.

The direct process of manufacturing sodium sulphate from common salt, sulphurous acid, and air, without the intervention of sulphuric acid, has been the subject of many efforts, commencing with Gossage's, in 1850. None of these had any practical success until Hargreaves and Robinson (beginning from 1870) introduced a number of improvements which have made that process practicable and successful. We shall here describe it in its improved form.

The process consists in conducting the gases from pyrites kilns of the usual type, mixed with a suitable quantity of steam, through a series of large cast-iron cylinders, charged with common salt, in such manner that the fresh gas meets with the salt which has been the longest time exposed to the treatment, whilst the nearly-exhausted gas is brought into contact with fresh common salt. In this way, on the one hand, the salt is completely converted into sulphate, and, on the other hand, the pyrites kiln gases are nearly as fully utilised as they would have been by passing them into vitriol-chambers. The reaction:

$$2NaCl+SO_2+O+H_2O=Na_2SO_4+2HCl,$$

takes place at a temperature of about 500°–550°C., and this must be maintained against the radiation into the surrounding space by external heating; but as the reaction itself produces heat, the amount of fuel required is not exorbitant—if care is taken to avoid undue loss of heat during the process. This is all the more necessary, as the process is a slow one: it takes from 2 to 4 weeks before the salt, charged into one of the cylinders, can be taken out in the shape of finished salt-cake.

The first step is bringing the salt into such a condition that the gases can readily pass through it and yet reach all parts of it to the very core. Salt of fine grain must be used, and usually either the salt known as 'butter salt' or powdered rock salt, or a mixture of both, is taken. A method of preparation generally adopted is as follows: The salt is crushed and moistened by water or exhaust steam. It then falls from a hopper upon an endless chain of plates, each about 12 ins. broad and 5 ft. across, of a tot length of about 100 ft., or more, rising up in a sloping oven and returning underneath. On falling upon that travelling-platform, the salt is mechanically beaten down into a layer of 1–1½ in. thickness, which is at once cut, by means of mechanically-moved knives, into cakes about 3½ ins. square. These now enter into an oven, which is heated by the waste heat of the cylinders or direct fire, and pass through it at such a rate that they arrive perfectly dry at the upper end. As the chain turns downwards the dry cakes detach themselves and fall down upon a grating. They are now dense enough to retain their shape in the cylinders, and to be handled without formation of any material quantity of dust, and yet porous enough to be entirely penetrated by the gases, their regularity of shape securing regularity of draught in the process.

It is of vital importance that uncaked or powdery salt shall not get into the cylinders, as if it does, it forms areas impermeable to the flow of the gases, and thus prevents the reaction from being completed.

The decomposition of the salt takes place in a series of cylinders, from 8 to 20 in number, about 15 ft. in diameter, and 12 ft. high, and holding 40 tons of salt-cake, or even more. They are surrounded by small vertical flues connected with a fireplace below, and their tops are protected against cooling by a thick layer of ashes. Inside there is a movable grate, on which the salt rests. A number of manholes in the top serve for charging; a large door above the bottom for discharging. A set of large cast-iron pipes serves to admit the burner-gas into any of those cylinders and for passing it through the whole series, the gas always entering at the top and going away at the bottom. The connections between the main gaspipe and any one cylinder and those between the single cylinders are opened or closed by a very simple arrangement—viz. by dividing the connecting elbow pipes or 'siphons' in two halves, and either shutting the connection by inserting an iron plate or else leaving it open, always luting the joint by a mixture of mortar and salt. From the last cylinder of the series the gases pass through an opening in the bottom of the drawing doorway, into a flue.

Fig. 29 shows such a set of 8 cylinders seen from the top. Fig. 30 shows the section of one of the cylinders. A_1 to A_8 are the cylinders, B the discharging doors, C C the iron pipes for burner-gas with their connecting siphons D and circulating siphons E; F is the outlet opening, G the gas-flue for the exit gas; J is an opening in the top by which cold air can be admitted, in case the cylinders get too hot through the heat of reaction.

The pyrites burners employed are specially constructed with a view to avoiding radiation and sending the gas as hot as possible into the cylinders. The necessary steam is superheated by the waste heat of the gases, and is usually introduced in the upper part of the burners.

The gases are drawn through the whole system by means of a Root's Blower or a cast-iron fan placed between the cylinders and the acid condensers. By keeping the blower so hot that no liquid acid can be condensed in it, it is protected against the action of the acid; but the ends of the shaft, passing through the blower, must, on the outside, run in water-cooled bearings. The exhaust steam of the engine is utilised for the steam required for mixing with the burner-gas.

The amount of fuel required in a special case was as follows (calculated upon 20 cwts. of salt-cake):

For heating cylinders . . .	4 cwts.
For preparing salt . . .	3 ,,
For steam	0·75 cwt.
	7·75 cwts.

In other cases nearly 10 cwts. of fuel has been required, but in any case no more fuel is needed than in the ordinary process of making sulphuric acid and employing this for decomposing the salt.

The amount of fuel required for heating the cylinders depends naturally on the construction of the plant, the care taken to avoid radiation losses and to get the pyrites gases as hot as possible into the leading cylinders. It also depends on the rate at which the plant is working. The more rapidly heat is generated in the cylinders the less the proportion of that heat which will be lost by radiation. The chemical composition of the salt has been held to materially affect the possible speed of working, and the evidence goes to show that other things being equal the salt containing the largest quantity of iron salts decomposes the most rapidly. This is the usually accepted explanation of the fact that the output of the same plant using powdered rock salt is greater than when using 'butter salt' which contains materially less iron.

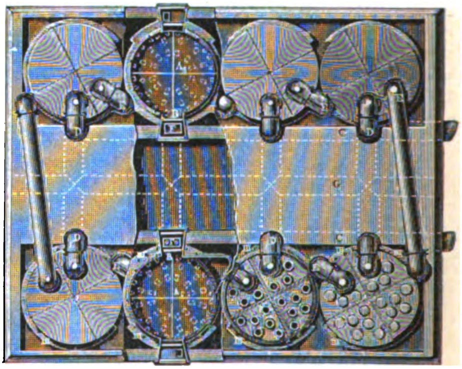

Fig. 29.

Hargreaves (Fr. Pat. 384144, 1907) promotes the reaction by the addition of 0·1–1·0 p.c. of copper or iron salts before moulding into cakes, the amount used depending on the purity of the product required.

In large well-designed plants when the speed of reaction is high no fuel is required to heat the cylinders. Great care is necessary in watching and controlling the temperature of the Hargreaves cylinders. If the later cylinders get too hot through the rapid action of strong hot sulphurous acid gases on the almost untouched salt, the salt itself will flux and form areas through which the gases cannot penetrate to complete the reaction.

The advantages of the Hargreaves process are a great saving in space and either, when making the same quality of salt-cake lower process costs than the sulphuric acid and salt process, or, with about the same process costs the power to make a higher grade salt-cake more free from iron than is possible in the ordinary process with the cast-iron decomposing-pan. The disadvantages are the great cost of the plant, which, unlike the lead vitriol chambers, does not return a large proportion of the initial cost on dismantling; the very careful supervision required with the consequent liability to serious difficulty and expense if the supervision even for a short time breaks down; and again the impossibility of utilising the hydrochloric acid gases evolved for the production of chlorine by the Deacon-chlorine process, owing to the quantity of sulphur dioxide and carbon dioxide they contain from time to time. This sulphur dioxide in the Deacon decomposers is fatal to the activity of the catalyst there used, viz. cupric chloride. The Hargreaves process is worked successfully in England in several manufactories, and also on the Continent, but has failed to extend materially in recent years.

Salt-cake free from iron (or nearly so) is required especially for plate-glass, window-glass, and so forth. The Hargreaves sulphate is frequently pure enough for this purpose. On the Continent it is sometimes made by employing decomposing pans made of lead, which are certainly much more difficult to manage than the cast-iron pots otherwise used. The batch must be taken out much thinner, and the firing must be much more careful than with cast-iron pots. Purified sodium sulphate is also made by dissolving ordinary salt-cake, precipitating the iron present by the addition of a little bleaching powder and lime and evaporating to dryness.

Glauber's salt is crystallised sodium sulphate $Na_2SO_4,10H_2O$. It is manufactured for a few purposes, principally for medicinal use and for freezing mixtures. A considerable quantity is obtained from the residuals of the Stassfurt salts, and from the mother-liquor in the manufacture of sea-salt. It is required in two very different states—viz. in very small or in large crystals. The small acicular crystals are obtained by making the solution as strong as possible at a temperature of 34°C., settling, running into shallow coolers, and stirring the solution until it has cooled down. The larger crystals ('soda fashion') are made by dissolving the sulphate at 50°, until the sp.gr. is 1·257 (at 40°), settling for an hour, and running into deep coolers (2–5 ft. deep), where the liquor is kept quite undisturbed. In order to facilitate the formation of large crystals, wooden staves or pieces of twine, weighted with a little lead, are hung in the vats. The cooling lasts from 5 to 20 days, according to the size of the vats and the season, the crystals are large (an inch and more thick), hard and shining, and they must be dried at a temperature not exceeding 30°, to prevent efflorescing.

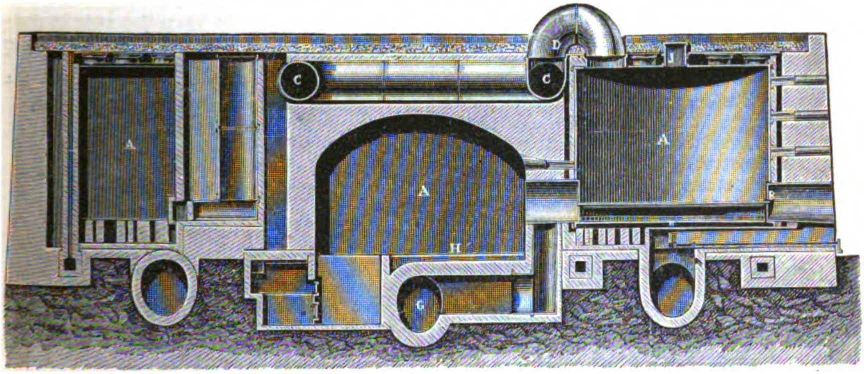

FIG. 30.

Testing of salt-cake.—It is usual in the factory to test the salt-cake only for free sulphuric acid and undecomposed sodium chloride, as these are the impurities over which the workman has control; the other impurities—iron, lime, alumina, &c.—depend on the quality of the salt used.

The usual methods of analysis adopted are given in Lunge's Technical Chemist's Handbook.

Two characteristic analyses of salt-cake are given below,

	Hand furnace salt-cake from white salt	Hargreaves salt-cake low in iron
Na_2SO_4 . . .	96·2	98·0
$NaCl$ . . .	0·5	0·2
H_2SO_4 . . .	1·5	0·3
$CaSO_4$ and insol. .	1·8	1·424
Fe_2O_3 . . .	—	0·076
	100·0	100·0

The chief uses of salt-cake are for the manufacture of caustic soda by the Leblanc process, for the manufacture of sodium sulphide and of glass. For the manufacture of practically all qualities of glass except lead glass, salt-cake is superior to soda ash because: It is cheaper per unit of alkali, and owing to the higher temperature at which the glass furnaces work when using salt-cake a higher proportion of silica can be used, thus again cheapening the cost and also producing a harder and more durable glass.

Sodium sulphide Na_2S. In practice sodium sulphide is always obtained by the reduction of sodium sulphate. The preparation of sodium sulphide has been the subject of much work and many patents. Arrot (Eng. Pat. 1370, 1859) Gossage (Eng. Pat. 2612, 1859), Wilson (Eng

Pat. 1361, 1859), Claus (Eng. Pats. 819 and 2616, 1869), Willans (Eng. Pat. 293, 1860), and Weldon (Eng. Pats. 3370 to 3390, 1876; and 444, 445, 1877). Winkler, in Chem. Ind. 1880, 129, gives a description of the method of making sodium sulphide in a small reverberatory furnace from a mixture of salt-cake and 25–30 p.c. of coal, which was in use for many years. Essp (Zeitsch. angew. Chem. 1889, 284) also describes the production of sulphide in a reverberatory furnace from salt-cake and 60 p.c. of coal-dust.

Gossage and Matheson (Eng. Pat. 3218, 1888) propose the mixing of a considerable quantity of NaCl with the salt-cake. Gossage and Williamson (Eng. Pat. 20921, 1892) proposed to add to the mixture of salt-cake and coal 35 or 40 parts of Leblanc black-ash waste in order to prevent the action on the furnace lining.

The Société Industriale de Pont Saint Martin and A. Piccinini (Zeitsch. angew. Chem. 1908, 782) prepare sodium sulphide in a kiln from coke and sulphate by heating the mixture in an electric furnace. Another interesting proposition is that of Gossage, Matheson and Hawlicek (Eng. Pat. 121480, 1886), who suggest the use of furnaces of the lime-kiln type for the production of sodium sulphide.

Ellershausen (Eng. Pat. 17815, 1890) describes the difficulties in maintaining the fabric of the furnace against the action of the sulphide, and ascribes them to the overheating of the charge. He constructs his furnace with a fire-bridge 2 ft. high above the furnace-bed, and avoids overheating the bridge by means of an internal air channel. The flue above the fire-bridge is contracted towards the centre of the furnace-bed, so that the sides do not get as hot as usual. The bed is also made to rise towards the bridge so that no melted sulphide can accumulate there. The sides of the furnace round the bed are made of firebricks in such a manner that they are independent of the outer walls, and are easily renewed. Lunge thus describes the working of this furnace from his personal observation (Sulphuric Acid and Alkali, vol. iii. p. 296): 'The charge consists of 7 cwt. salt-cake, and 3½ cwt. coke breeze, not specially mixed, but put in the usual way, first upon the back bed and brought there to a dark red heat without any fusion. The fusion takes place on the front bed, where the mass turns first thin and then again thickens, just like an ordinary black-ash charge, but without exhibiting the well-known 'candles.' It is, however, not so pasty as black-ash, and more porous. It is drawn out into an iron box after first lowering the furnace damper to prevent its burning during the discharging. The mass cools down in these boxes without any special precautions. Sixteen such charges are finished during 24 hours with a consumption of 1¼ tons of coal. The heat is not so high as in black-ash furnace, and the furnaces do not require much repair. . . . It is very remarkable that in this case the furnace bottoms did not suffer very much, seeing that they were made exactly like those of black-ash furnaces (*see* Leblanc Soda Process, p. 39), except that they were a little sloping from the firebridge; the slope towards the working door is common to both. The reason is probably this, that with the large quantity of small coke 50 p.c. the mass always remains porous; the infusibility of coke is also an advantage in comparison with ordinary mixing coal. During work the damper must always be kept down as much as possible to avoid unnecessary entrance of air; if this is not done the mass turns more liquid, evidently by the formation of polysulphides, and the furnace suffers much more. The crude sulphide on analysis shows only a trace of polysulphides, no sulphate at all, about 1½ p.c. thiosulphate, and about 10 p.c. of the soda as carbonate, the remaining soda being present as Na_2S; there is about 25 p.c. insoluble. This is certainly an excellent product.'

The crude sulphide or sulphide 'black-ash,' was, after cooling, originally broken up into lumps, packed and sold. One or two cases, however, of fire on board ship occurred which were attributed to spontaneous combustion of the crude sulphide, and carriage in this form was stopped (J. Soc. Chem. Ind. 1896, 838). The crude sulphide is now all lixiviated in vats similar to those described under the Leblanc process for lixiviating Leblanc 'blackash' (*see* Figs. 34 and 35), the only difference being that it is necessary to keep the vats in the case of sulphide much hotter than in the case of Leblanc soda (*see* p. 43).

The vat liquor, after settling, is run into crystallising cones and allowed to cool, when crystals of $Na_2S,9H_2O$ separate out of approximately the following composition:—

Na_2S	32·0 p.c.
$Na_2S_2O_3$	1·4 „
Na_2SO_3	1·4 „
H_2O (by diff.) . . .	65·2 „
	100·0 „

The crystals after well draining are packed in casks.

Sodium sulphide is moderately soluble in water, and crystallises in white, quadratic crystals, of sp.gr. 2·471, which contain 9 mols. of water. Other hydrates have also been described (Parravano and Fornaini, Gazz. chim. ital. 1907, 37, ii. 521); *see* Göttig (J. pr. Chem. 1886, 34, [ii.] 229), Abstinthe (J. Soc. Chem. Ind. 1886, 534).

The aqueous solution of the salt reacts strongly alkaline owing to hydrolysis. A more concentrated form of sodium sulphide is made by concentrating the vat liquor usually in the so-called caustic pots. The liquor is concentrated until the temperature rises to about 160°, when a sample will be found to test 60 p.c. Na_2S. The fire is then drawn and the pot allowed to settle for 4–6 hours, and then the sulphide is packed in an exactly similar way to caustic soda into the ordinary caustic soda drum (*see* Fig. 43).

The sulphide so prepared has the following composition:—

Na_2S	62·8 p.c.
$Na_2S_2O_3$	2·9 „
Na_2SO_4	1·1 „
NaCl	1·7 „
Fe_2O_3	0·44 „
Water (by diff.) . .	31·06 „
	100·0 „

The concentrated sulphide is also put on th market in disks 2–4 ins. thick and in broken pieces of various sizes.

It will be observed that the concentrated sulphide contains over 30 p.c. of water. It has been found by experience that this quantity of water entirely prevents all danger of the spontaneous combustion mentioned above as being traced to the impure anhydrous sulphide packed direct from the furnaces.

Sodium sulphide is largely used as a depilatory in the tanning industry, and in the colour industry as one of the raw materials of the so-called sulphur colours, and as a solvent of these colours in the dye-bath. It is also used in the manufacture of water-glass.

A disulphide, trisulphide, tetrasulphide, and pentasulphide of sodium have also been prepared. *See* Böttger (Annalen, 1884, 223, 335, 338), Locke and Anstell (Amer. Chem. J. 1898, 20, 592), and Hugot (Compt. rend. 1899, 129, 388).

Sodium thiosulphate (hyposulphite)

$Na_2S_2O_3,5H_2O$.

This compound was first prepared in 1799 by Chaussier. Small quantities of the salt may be made by taking about 1 lb. of pure, well-dried sodium carbonate, mixing with it about one-third its weight of flowers of sulphur, and then heating the mixture in a porcelain basin to the melting-point of sulphur for some time, stirring well all the while, so as to bring every part in contact with the air. Oxygen is absorbed by the sodium sulphide formed, which is converted, with feeble incandescence, into sodium thiosulphate. When cold, the mass is dissolved in water, boiled with sulphur for some time, and the liquid concentrated by evaporation to the crystallising-point. A very pure product may be thus obtained. It can be prepared by boiling a solution of sodium sulphite with flowers of sulphur, filtering from the excess of the latter, and allowing the solution to crystallise. Another method consists in boiling sulphur with soda-lye and passing sulphur dioxide into the yellow solution until it becomes colourless. The anhydrous salt is easily prepared by passing air over anhydrous NaSH at a temperature of 100°–150°.

The earthy thiosulphates are obtained by exposing their sulphides to the oxidising action of the air; and upon this principle depends Losh's process, which is as follows: The tank waste produced in alkali works is exposed to the air for a week or more, being turned over from time to time, so as to bring every portion in contact with air. The mass is then lixiviated with water, and, on adding sodium carbonate solution to the dissolved thiosulphates of sodium and calcium, the calcium is precipitated as carbonate, and the whole of the thiosulphuric acid is converted into the sodium salt. The solution is drawn off from the insoluble precipitate, concentrated by evaporation, and the crystals of sodium thiosulphate purified by recrystallisation. A modification of this process, by Kopp, is as follows: The tank waste is mixed with 10–15 p.c. of sulphur and 12-15 times its weight of water, and is then boiled for an hour. The solution of polysulphide obtained is put into a closed apparatus, in which it can be agitated, and is treated with sulphur dioxide. The solution now contains calcium thiosulphate, and is converted into the sodium salt by addition of sodium sulphate. The solution of sodium thiosulphate is drawn off from the precipitate of calcium sulphate, and is concentrated and crystallised as before. Another method consists in allowing the liquid extract of the oxidised tank-waste to run down a tower packed with coke, where it meets with a strong upward current of air. A little steam is also injected into the tower. The polysulphides are by this treatment oxidised to thiosulphates. The solution running away from the bottom of the tower has an acid reaction, and is neutralised with milk of lime, evaporated to a sp.gr. of 1·25, and a solution of sodium sulphate added until the precipitation of the calcium is complete. The precipitate, consisting chiefly of calcium sulphate, but containing also from 2 to 5 p.c. sodium and calcium sulphites and thiosulphates, is dried at 100°, and sold to the paper makers, the calcium sulphate serving as a weighting material and the sulphites, &c., it contains acting as an antichlor. The filtered solution is evaporated to a sp.gr. of 1·65 and allowed to cool, when sodium thiosulphate and a little sulphite crystallise out.

The yield of thiosulphate can be greatly increased by suitable treatment. Schaffner (Dingl. poly. J. 193, 42) treats the yellow sulphide liquors with sulphur dioxide, exactly neutralises the excess of the latter by the addition of a further quantity of fresh sulphide liquor, heats to 75°–90°, and adds the requisite amount of sodium sulphate (determined by the analysis of a sample of the liquid). Finally, a little caustic soda is added to ensure the complete precipitation of the calcium sulphate. If traces of sulphides are still present they are removed by the addition of a little sodium bisulphite, and the clear solution is then evaporated to 43°Beaumé and allowed to crystallise. The crystals so obtained are sold directly for use as an antichlor, but if required for photographic purposes they are recrystallised once in stoneware pans.

The preparation of sodium thiosulphate has been carried out as follows: Strontium sulphide —obtained by reducing strontium sulphate by means of powdered coal—is, while still hot, mixed with water to form a thin paste. The mass is boiled with sufficient caustic alkali to combine with the sulphur of the sulphide. Strontium hydroxide crystallises out on cooling, and the mother-liquor consists of solution of sodium sulphide. On treating this liquor with sulphur dioxide, sodium thiosulphate is formed, and free sulphur deposited (J. Soc. Chem. Ind. 3, 30).

Another process consists in the reduction of sodium sulphate by furnacing with coal, the extraction of the Na_2S so obtained by water, and the treatment of this sulphide solution with sulphur dioxide.

Sodium thiosulphate may also be prepared from the spent lime of the purifiers of gas works, which contains the calcium salt of thiosulphuric acid as well as calcium sulphide.

Other patents for the technical manufacture of sodium thiosulphate are given briefly below:—

Verein Chemischer Fabriken zu Mannheim, Eng. Pat. 23217 *b* and *c*, 1907 (air is passed over anhydrous NaHS at 100°–150°); Sidler, D. R. PP. 81437 and 84240 (sodium sulphite is heated with fused sulphur in CO_2); Verein Ch. Fab. zu Mannheim, D. R. P. 88594 (production of sodium thiosulphate by the action of SO_2 and steam on a mixture of $NaHSO_3$ and S in presence of water); Clemm, D. R. P. 180554 (manufacture of sodium thiosulphate from bauxite).

The salt forms large transparent prisms, belonging to the monoclinic system. Its solution is neutral to test paper; it is without smell, has a cooling taste, and does not change on exposure to air. The crystals melt in their water of crystallisation at 45°, all the water being expelled at 215°; and at 220° they decompose, with separation of sulphur (Pape). The salt has a sp.gr. of 1·672.

It dissolves very readily in water with considerable absorption of heat. It easily forms supersaturated solutions, which may be made to contain as much as 217 parts of the salt in 100 of water at 0°. It is insoluble in alcohol. The aqueous solutions of the salt have a neutral reaction and are permanent in the absence of air and light. Freshly made dilute solutions commonly alter in strength at first owing to the action of the carbon dioxide, usually present in water, on the salt; hence in preparing a solution of sodium thiosulphate for analytical purposes it is necessary to allow it to stand for a week before standardising it. After all the carbon dioxide present in the water has reacted with the salt the solution may be kept almost indefinitely without further alteration. The solution has the property of dissolving many insoluble salts, such as lead sulphate and silver iodide. Besides the commonly occurring pentahydrate a large number of other hydrates have been prepared and studied by Young, Mitchell, and Burke (J. Amer. Chem. Soc. 1904, 26, 1389 and 1413; 1906, 28, 315).

Sodium thiosulphate is used as an antichlor for removing the last traces of the chlorine from bleached fabrics, the reaction being essentially—

$$Na_2S_2O_3+4Cl_2+5H_2O=2NaCl+2H_2SO_4+6HCl$$

According to Lunge (Bolley's Technologie, Neue Folge, 1909, 16, 74) only about one-tenth of the amount of chlorine required by the above equation is acted upon, as a large quantity of tetrathionate is formed, while a further portion of the thiosulphate is probably decomposed into trithionate and sulphide—

$$2Na_2S_2O_3=Na_2S_3O_6+Na_2S$$

since some sulphuretted hydrogen is always evolved.

Sodium thiosulphate finds an extended application in photography. Owing to its power of dissolving silver bromide, iodide, &c., a solution of the salt is employed to dissolve out the unaltered silver halogen compound from the plates or prints after the exposure has been made and the image developed, the negative or print being thus 'fixed' and rendered unalterable on exposure to light. It is also used in the bleaching of wool, straw, oils, ivory, bones, &c. (as a source of SO_2), and as a preservative against fermentation in the sugar industry. In the calico-printing and dyeing trades it is employed in the preparation of mordants; aluminium sulphate is treated with sodium thiosulphate, and the resulting solution of aluminium thiosulphate thickened as usual and printed on the fibre. On steaming the printed cloth alumina is deposited on the fibre by the decomposition of the aluminium thiosulphate, and the material can then be dyed with alizarin, &c. It has been used to fix aniline greens, and in conjunction with salts of copper to produce the so-called 'argentine effects' which depend upon the deposition of a thin film of copper sulphide on the fibre. Sodium thiosulphate is also employed in the preparation of various artificial colours, and in the reduction of indigo; in the wet methods of preparation of antimony cinnabar, and ordinary cinnabar; in metallurgy for wet silver-extraction processes, the silver being converted into chloride by roasting the ore with common salt, and the mass lixiviated with a solution of the sodium thiosulphate (*v.* SILVER); in the preparation of silvering and gilding solutions, and in the extraction of gold from ores. When treated with sodium amalgam, it gives sodium sulphide and sulphite:

$$Na_2S_2O_3+Na_2=Na_2SO_3+Na_2S.$$

The property which the salt possesses of fusing at a low temperature in its water of crystallisation and solidifying again on cooling has been utilised by Fleck in sealing glass tubes containing explosives to be used under water in torpedoes.

In medicine sodium thiosulphate is used in cases of sarcinous vomiting, and as an external application in parasitic skin diseases.

In the laboratory the salt is largely used in iodometry, the fundamental reaction being—

$$2Na_2S_2O_3+I_2=Na_2S_4O_6+2NaI.$$

For the application of this *see* the article on ANALYSIS. It has also been proposed for use in quantitative analysis for the precipitation of various metals in place of sulphuretted hydrogen. Lead, mercury, silver, copper, and chromium are all quantitatively precipitable as sulphides (or in the case of chromium as hydroxide) by boiling their solutions with sodium thiosulphate (Faktar, Zeitsch. anal. Chem. 1900, 39, 345).

Sodium thiosulphate is employed in the separation of iron and aluminium. A solution containing these two metals is treated in the cold with sodium thiosulphate; this gives rise to the aluminium thiosulphate, and, when boiled, the latter is decomposed, with evolution of sulphur dioxide and deposition of sulphur and alumina. By throwing the whole on a filter, the iron, still in solution, passes through.

Sodium thiosulphate forms a large number of double salts, many of which are of extremely complex composition. Those formed with copper and silver have been studied by Rosenheim and Steinhäuser (Zeitsch. anorg. Chem. 1900, 25, 72) and C. and I. Bhaduri (*ibid.* 1898, 17, 1). *See* also L. Shinn (J. Amer. Chem. Soc. 1904, 26, 947).

Sodium nitrite $NaNO_2$ occurs native in small amounts in Chile saltpetre, and is frequently found, although only in traces, in mineral waters. It can be prepared artificially by heating sodium nitrate, either alone or mixed with deoxidising substances, metallic lead, iron filings, or graphite being those usually employed. The salt prepared in this way, however, invariably contains some caustic soda and undecomposed nitrate. The pure salt is best made by decomposing a solution of silver nitrite with an equivalent amount of sodium chloride, or by passing the nitrous fumes evolved from a mixture of nitric acid and starch into a solution of caustic soda or sodium carbonate (Divers, Chem. Soc. Trans. 1899, 86).

It may also be obtained by the electrolytic reduction of the nitrate, but the yield obtained is only 60 p.c. of the theoretical (Muller, Zeitsch. Elektro. Chem. 1903, 9, 955).

Technical manufacture. On the large scale, sodium nitrite is made by the reduction of the nitrate, usually with metallic lead.

The lead employed must be as free as possible from zinc and antimony, and is rolled out into thin sheets previous to use. The theoretical amount of lead required for the decomposition of 100 parts of sodium nitrate according to the equation—

$$NaNO_3+Pb=NaNO_2+PbO$$

is 243 parts, but in practice an excess is invariably used.

The sodium nitrate (100 kilos.) is melted in a cast-iron vessel fitted with a mechanical stirrer. As soon as the whole is in a state of quiet fusion, 250 kilos. of lead are added, which rapidly oxidises to yellow PbO. After a short time more lead is added, and the mixture kept well stirred for three-quarters of an hour, the whole operation lasting about 3½ hours. Thorough stirring is essential, as if any of the mixture is allowed to cake on the sides of the vessel, the latter is soon corroded and rendered useless.

The product from the fusion (which should contain over 90 p.c. of $NaNO_2$) is extracted with water in wrought-iron vessels, provided with stirrers, until the solution has a density of 36°–39° Beaumé. The alkaline liquid is then carefully neutralised with dilute nitric acid, and allowed to settle. The clear solution is evaporated to 42°–43° Beaumé, allowed to stand three or four hours to clarify, and then run into lead-lined wooden tanks where crystallisation takes place. The crystals obtained contain, after being dried at 60°, 97–98 p.c. of sodium nitrite.

The mother-liquors can be evaporated several successive times after addition each time of a little fresh liquid from the vats. The purity of the nitrite thus obtained continually diminishes, as the following figures show :—

	Percentage of $NaNO_2$ contained in the crystals after drying at 60°.
Crystals from 1st evaporation	97 to 97·5 p.c.
„ 2nd „	96·8 to 97 „
„ 3rd „	96·2 to 96·5 „
„ 4th „	96 to 96·2 „

If a higher content of nitrite be required, the salt must be recrystallised. When the crystals obtained from the liquid show less than 96 p.c. of $NaNO_2$, the mother-liquor is evaporated separately in a second pan, and produces crystals containing 86–94 p.c. of nitrite, which are employed to strengthen the fresh lye. The solution separated from these is further concentrated in a third pan, and yields crystals containing 50–75 p.c. of nitrite. Those containing above 65 p.c. $NaNO_2$ are returned to the second pan, and the remainder are fused up again with lead in the manner described above. An analysis of the final mother-liquors gave their composition as :—

	p.c.
Caustic soda	10·89
Sodium carbonate	22·00
Sodium nitrite	20·52
Sodium nitrate	16·23
Sodium chloride	6·05
Sodium sulphate	17·39
Insoluble	7·23
	100·31

Another process for making sodium nitrite consists in fusing together 500 kilos. sodium nitrate and 500 kilos. caustic soda, adding 225 kilos. iron filings, and allowing the mass to react for 5–6 hours. Various other reducing agents, such as sulphur, calcium sulphide (tank-waste), barium sulphide, zinc blende, and galena have also been employed.

Properties. Sodium nitrite forms small rhombic crystals, which usually possess a faint yellow colour, although according to Boguski (J. Russ. Phys. Chem. Soc. 1899, 31, 543) the pure dry salt is colourless. The crystals melt at 271° (Divers) and dissolve easily in water (1 part of the salt dissolves in 1·2 parts of water at 15°) forming a yellowish solution which is alkaline to litmus. The salt is very sparingly soluble in absolute alcohol, 100 parts of this solvent dissolving only 0·31 part of sodium nitrite at 19·5°.

For the density of sodium nitrite solutions, *see* Boguski, Anz. Krak. Akad., 1898, 123. For conductivity measurements, *see* Roczkowsky and Niementowsky, Zeitsch. physikal. Chem. 1897, 22, 147, and Schumann, Ber. 1900, 33, 532.

Uses. Sodium nitrite is largely used in the manufacture of coal-tar colours, and also in the calico-printing industry in the preparation of certain colours, such as paranitraniline red, which are developed on the fibre.

Sodium nitrate (*cubic nitre*; *Chile saltpetre*) $NaNO_3$. This important salt occurs as *nitratine* in the natural and artificial accumulations of potassium nitrate, and in other deposits where it has been produced similarly to that salt (*v. Potassium Nitrate*, art. POTASSIUM).

The natural occurrence of the sodium nitrate, as distinguished from the potassium salt, does not appear to have been fully recognised until the present century, for it is stated in Rees' Encyclopædia, 1819 (art. NITRATE OF SODA), that it had not been found up to that time in a native state, although its manurial value had already been recognised by Lord Dundonald.

Sodium nitrate occurs in enormous quantities, and practically free from the potassium salt, in the province of Tarapaca in South America, and this, with the exception of certain deposits on the coast of Bolivia, constitutes the only source from which the salt is extracted on the large scale.

The nitrate deposits do not form beds of any definite character, but represent the outcrop of a bed of salt which appears to have been left at the bottom and sides of ancient tidal lagoons by the upheaval of the coast. Although the district is now extremely arid and only receives rain at intervals of 3 years or more, there is abundant evidence of former fertility in the large quantities of buried trees and other vegetation which are found in the vicinity, together with guano and fish remains, sea-shells, and other substances of marine origin.

The nitrate may be regarded as the product of the decomposition of this organic matter in presence of calcium carbonate and the salt left by the evaporation of the sea-water. This view is borne out by the composition of the deposit, especially by the presence of sodium iodide and iodate and of salts of magnesium and calcium. The nitrification appears to have occurred only at the outcrop of the salt, for the nitrate diminishes in quantity towards the middle, and is practically absent at the centre of the deposit.

The main nitrate belt of Tarapaca has a width of about 2½ miles, and is included between latitudes 27°S. and 19°S. for a total length of about 260 miles. It stretches along the eastern slope of the coast range of the mountains which extend from the northern limit of Peru to the Straits of Magellan, and which have an average height of about 2000 ft.

The deposit occurs some 500 or 600 ft. higher than the valley of Tamaragal, and diminishes in richness as the valley is approached, the nitrate disappearing altogether at the bottom. The average distance from the sea coast is about 14 miles, but some of the deposits are as far distant as 90 miles.

The 'caliche,' as the crude nitrate is called, is never found at any great depth. It is usually covered to a depth of 6 or 10 feet by a crust or 'costra,' consisting of a conglomerate of porphyry, felspar, magnesia, sodium chloride, &c., cemented together by gypsum, and covered by a layer of fine loose sand to a depth of 8 or 10 ins. The caliche proper forms a rock-like mass from 3 to 6 ft. deep, and varies in colour from almost pure white, through shades of yellow, orange, brown, bluish-grey, &c. The lower part of the caliche (known as 'congelo') contains but little nitrate, and abounds in the chlorides of sodium and magnesium, and in sulphates. It lies upon a pale, yellowish-brown, loose clay free from nitrate, and overlying the primitive rock.

Various qualities of caliche are worked, varying from 40 to 80 p.c. in the best quality, to 30 to 40 p.c. in the second, and 17 to 30 p.c. in the inferior kinds.

A good ground would contain a bed 3–4 ft. thick, containing 40–45 p.c. $NaNO_3$. The upper overlayer varies from 4 to 20 p.c. In poor grounds, however, 20 p.c. nitrate would become 'caliche.' The ground is broken by blasting and the big blocks divided into smaller ones with crowbars and the lumps of 'caliche' separated from the overlayer or 'costra' by hand.

The Tarapaca deposits were worked as early as 1813 by the Spaniards, who exported 23,732 quintals (of 100 pounds) in that year; but the industry was but little developed until 1852, when small refining works were established by Smith and Sandes.

The method of separating the nitrate from the caliche consists merely of a careful system of lixiviation. At the Officina of Ramirez (Tarapaca) the caliche is crushed roughly into 2-in. lumps, and is boiled in long tanks heated by steam coils.

A typical boiling tank is 32 ft. long by 9 ft. deep by 6 ft. wide, and is heated by a steam coil 5 ins. diameter, which makes the circuit of the tank five times, and is arranged in tiers about 9 ins. from the sides. The 'caliche' is supported on a false bottom about 1 ft. from the real bottom of the tank. The tanks are built in a series of six, connected by a 9-in. pipe for circulating the liquor from one to the other. The tank containing the nearly exhausted 'caliche' is fed with fresh water, the others work in series with weak liquor obtained from the nearly exhausted tank, passing through them and leaving finally from the tank last charged with 'caliche.' The hot liquor or 'caldo' finally runs off at 112°, containing about 80 lbs. nitre to the cubic foot. After cooling for 4 or 5 days in the crystallisers and crystallising out, the strength of the liquor is reduced to about 40 lbs. nitre per cubic foot. This mother-liquor is used in the systematic lixiviation of the 'caliche' described above, and is run in addition to the weak liquor from final exhaustion of the 'caliche' on to the later tanks.

A good form of crystalliser is a sheet-iron tank 25 ft. by 18 ft. by 2 ft. 9 ins. to 3 ft. deep, the inclined bottom assisting in the draining of the crystals. Six such tanks as have been described require about 44 of these crystallising vessels.

The nitrate from the crystallisers is drained and is placed on the drying floor to dry for 5 or more days, when its composition is as follows:—

	First quality	Second quality
$NaNO_3$ . .	96·5	95·2
$NaCl$ . .	0·75	2·5
Na_2SO_4 . .	0·45	0·6
H_2O . .	2·3	1·7

An important by-product in the Chile nitrate industry is iodine, which occurs in considerable quantities as sodium iodate in the 'caliche.' The iodine recovery is effected from the mother-liquor from the crystalliser which passes through the iodine house on its way back to the lixiviating tanks (*v.* IODINE). The fuel consumption averages about 1 ton coal to 7 tons nitrate produced.

For further details of the nitrate manufacture, *see* paper by Newton, J. Soc. Chem. Ind. 1900, 408, from which most of the above statements have been taken.

The following analyses show the composition of caliche. (1) Shows the composition of one of the largely-worked deposits (Forbes, Phil. Mag. 1866, 32, 135); (2) shows the composition of that worked at the Officina Ramirez (Harvey, Proc. Inst. C.E. 1885, 82, 337):—

	(1)	(2)
Sodium nitrate .	21·01	51
Sodium chloride .	55·27	26
Sodium sulphate .	4·74	6
Calcium chloride .	0·33	—
Potassium iodide .	0·87	—
Aluminium sulphate	9·81	—
Magnesium sulphate	5·93	3
Insoluble matter .	2·04	14
Moisture . .	—	—
	100·00	100

Further information on these deposits will be found in the works of Sturzer (Nitrate of Soda, 1887; edited by Wagner) and Billinghurst (Estudio sobre la Geografia de Tarapaca, and Chem. Zeit. 11, 752), and in the various Consular reports to the British and United States Governments.

Sodium nitrate is obtained when sodium carbonate or hydroxide is dissolved in nitric acid, or when common salt is boiled with that acid. On the large scale, however, it is always obtained from the natural product by repeated crystallisation. The last traces of chloride are best removed by adding a small quantity of nitric acid to the boiling saturated solution of the salt, and recrystallising.

The pure salt forms transparent, colourless, anhydrous rhombohedra, whose angles closely approximate to right angles, whence its name 'cubic nitre.' It fuses at 316° (Carnelley, Chem. Soc. Trans. 33, 276); at higher temperatures—lower than that at which potassium nitrate decomposes—it evolves oxygen with production of the nitrite, and on further heating it gives off nitrogen and nitrous fumes, leaving a residue of sodium monoxide and peroxide. The salt as usually obtained is hygroscopic; but, according to Gentele (Dingl. poly. J. 118, 203), this is due to the presence of the nitrates and chlorides of calcium and magnesium, and is not observable in the pure salt.

According to Ditte (Compt. rend. 80, 1164) 100 parts of water dissolve the following proportions of the salt:—

At 0°	66·69	At 18°	83·62
2°	70·97	21°	85·73
4°	71·04	26°	90·33
8°	75·65	29°	92·93
10°	76·31	36°	99·39
13°	79·00	51°	113·63
15°	80·60	68°	125·07

When saturated at 0° the solution may be cooled to −15·7° without crystallisation; but at that temperature the salt separates out in fine laminated plates built up of fine needles lying side by side. A hydrate of the composition $NaNO_3,7H_2O$ appears to exist (Ditte, *l.c.*).

Sodium nitrate dissolves in glycerol, but is almost insoluble in absolute alcohol; 100 parts of alcohol of 16·4 p.c. dissolve 21·25 parts of the salt (Pohl, Sitz. Ber. 6, 600).

It is used for many of the purposes for which the potassium salt is employed; but its hygroscopic nature renders it inapplicable to the manufacture of gunpowder or fireworks, &c. For the making of nitric acid, for supplying that acid in the sulphuric acid manufacture, and as a manure, it has, however, entirely replaced potassium nitrate. It is also the principal source of that salt, which is obtained from it by double decomposition with the potassium chloride of Stassfurt.

Sodium hypophosphite NaH_2PO_2 may be prepared by boiling aqueous or alcoholic soda with phosphorus until evolution of phosphoretted hydrogen ceases

$$6NaHO+2P_4+6H_2O=6NaH_2PO_2+2PH_3.$$

The solution is poured off, treated with sodium bicarbonate to convert any unchanged soda into carbonate, and is evaporated and digested with absolute alcohol, which dissolves the hypophosphite only. The salt crystallises out on cooling.

For pharmaceutical purposes it is usually prepared by double decomposition between solutions of sodium carbonate and calcium or barium hypophosphite (*v. Phosphorus oxides* and *Oxy-acids*, art. PHOSPHORUS). The filtered solution is evaporated on the water-bath with frequent stirring as the mass becomes syrupy, in order to obtain a granular salt. To obtain the salt free from phosphite, Raymond (Pharm. J. [iii.] 10, 407) treats 25 grms. of the commercial salt with 1 grm. of barium hypophosphite in solution, and dilutes to 50 c.c., adding 200 c.c. of strong alcohol after a time. The liquid is allowed to stand and filtered from the precipitated barium phosphite and hypophosphite, and the last traces of barium having been removed by careful addition of sodium nitrate, is filtered and mixed with 500 c.c. of strong alcohol and a sufficiency of ether. The pure hypophosphite which separates is dried in a current of air.

Sodium hypophosphite crystallises in small, pearly, rectangular, very deliquescent plates containing 1 molecule of water of crystallisation. It dissolves at 15° in 1 part of water, and at 100° in 0·12 part. It is also soluble in alcohol. The aqueous solution absorbs oxygen from the air with formation of phosphite (Wurtz, Ann. Chim. Phys. [iii.] 7, 37).

When heated to 200° the crystals become anhydrous, and on further heating are converted into metaphosphate and pyrophosphate, with evolution of hydrogen and spontaneously inflammable phosphoretted hydrogen:

$$5NaH_2PO_2=Na_4P_2O_7+NaPO_3+2PH_3+2H_2.$$

It explodes when triturated or heated with an oxidising agent, and has been known to explode during evaporation on the water-bath (Amer. J. Pharm. 1860, 87).

Sodium hypophosphite is a powerful reducing agent, and precipitates gold and silver from solution. With copper salts it gives a red precipitate of copper hydride Cu_2H_2. It is used medicinally.

Sodium phosphates. A considerable number of these salts belonging to the three classes ortho-, pyro-, and meta- phosphates, together with a large series of double salts, are known. The three classes of salts may be distinguished by their behaviour with silver nitrate and albumen. The orthophosphates give a yellow precipitate with the former, while the pyro- and meta- phosphates give a white precipitate; and the metaphosphate alone gives a precipitate with albumen.

Our knowledge of the various sodium phosphates is largely due to Graham (Phil. Trans. 1833, 253). The metaphosphates have been particularly examined by Maddrell (Chem. Soc. Mem. 3, 373).

Several highly-complicated phosphates not belonging to any of these classes are also known. Thus Fleitmann and Henneberg (Annalen, 65, 304) have obtained peculiar phosphates, one of which has the composition $Na_6P_4O_{13}$, by fusing tetra-sodium pyrophosphate with sodium monometaphosphate, and Filhol and Senderens (Compt. rend. 93, 388) have obtained a phosphate of the composition $(NaHO)_3(P_2O_5)_2,H_2O$ by adding soda to a solution of orthophosphoric acid until neutral to colour tests.

Three orthophosphates, respectively containing one, two, and three atoms of sodium in the molecule, are known.

Trisodium orthophosphate Na_3PO_4 is obtained by adding excess of caustic soda to hydrogen sodium phosphate, and crystallising to remove the free alkali. It may also be prepared by fusing hydrogen disodium phosphate with excess of soda and dissolving and crystallising. It forms non-efflorescent six-sided prisms of the composition $Na_3PO_4,12H_2O$. According to Mohr (Amer. J. Sci. [iii.] 14, 281), their sp.gr. at 17·5° is 2·5362. They fuse at about 73·4°; at 100° they lose 11 molecules, but they retain the last until the heat approaches redness. A hepta- and decahydrate have also been prepared. The hydrated salt dissolves in about 10 times its weight of water at 15°. The solution reacts strongly alkaline in consequence of the salt being hydrolysed to a great extent into Na_2HPO_4 and NaOH. In solutions weaker than decinormal almost the whole of the salt is thus decomposed (Salm, Zeitsch. physikal. Chem. 1907, 57, 471; Shield, *ibid.* 1893, 12, 167). In consequence of this hydrolysis a solution of the salt is decomposed by all acids, even by CO_2, with formation of disodium phosphate and the salt of the acid in question. Tribasic sodium phosphate is used in place of sodium carbonate in some photographic developers, and it has been proposed to use the melting-point of the dodecahydrated salt (73·4°) as a standard for use in calibrating thermometers.

Hydrogen disodium phosphate Na_2HPO_4 occurs in urine, in which it was discovered by Haupt in 1740, and was at one time prepared from it under the name *sal mirabile perlatum.* It may be prepared by adding sodium carbonate to phosphoric acid until alkaline, and filtering, concentrating, and crystallising the solution.

It is usually prepared from the acid calcium phosphate made by the action of sulphuric acid on bone ash. For this purpose the hot solution is treated with sodium carbonate until effervescence ceases, and the solution of hydrogen sodium phosphate thus produced is filtered from the precipitated tricalcium phosphate, and is concentrated and crystallised.

The salt crystallises in large, colourless, transparent monoclinic prisms of the composition $Na_2HPO_4,12H_2O$. They soon effloresce, forming the heptahydrate, and become opaque on exposure to the air.

They melt at 35° (Tilden, Chem. Soc. Trans. 45, 268), and have a sp.gr. of 1·5235 at 15° (Stolba, J. Pharm. Chim. 97, 503). When dried over sulphuric acid, or heated for some time to 45°, they become anhydrous.

On further heating sodium pyrosphophate is formed, the transformation being complete at 300°:

$$2Na_2HPO_4=Na_4P_2O_7+H_2O.$$

Sodium phosphate dissolves readily in water, easily forming supersaturated solutions. The solubility of the salt at different temperatures has been determined by Mulder (Scheidekund Verhand. 1864, 100).

Temp.	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	99°
Parts Na_2HPO_4 per 100 of water	2·5	3·9	9·3	24·1	63·9	82·5	91·6	95·0	96·6	97·8	98·8

The saturated solution boils at 105°. The salt does not dissolve in alcohol. Its aqueous solution reacts alkaline due to slight hydrolysis.

According to Poggiale (J. Pharm. Chim. [iii.] 44, 273), 100 parts of water dissolve the following amounts of the anhydrous salt:—

0°	1·55	60°	55·29
10°	4·10	70°	68·72
20°	11·08	80°	81·29
30°	19·95	90°	95·02
40°	30·88	100°	108·20
50°	43·31	106·2°	114·43

When evaporated at 33°, it deposits monoclinic crystals of the composition

$$Na_2HPO_4,7H_2O.$$

Hydrogen disodium phosphate is used in certain photographic toning solutions, and to some extent in calico-printing and for weighting silk.

Sodium dihydrogen phosphate NaH_2PO_4 is prepared by adding phosphoric acid to a solution of the disodium salt until the liquid ceases to give a precipitate with barium chloride. It is obtained on cooling the hot strong solution in rhombic crystals of sp.gr. 1·90, containing 2 molecules of water, which are very soluble in water but insoluble in alcohol. A hydrate NaH_2PO_4,H_2O has also been prepared. On heating to 100° the salt becomes anhydrous, at 210° it is converted into the acid pyrophosphate $Na_2H_2P_2O_7$, and on further heating yields a mixture of metaphosphate and trimetaphosphate (Knorre, Zeitsch. anorg. Chem. 1900, 24, 369).

Many double orthophosphates containing sodium are known, the most important being 'microcosmic salt' $Na(NH_4)HPO_4,4H_2O$, which occurs in urine. It was well known to the alchemists under the names of 'microcosmic salt,' 'fusible salt of urine,' and 'essential salt of urine,' and was employed by them as a source of phosphorus. It has also been met with in nature as the mineral *stercorite*, found in some guano deposits.

The salt is obtained artificially by mixing hot solutions of 5 parts disodium phosphate and 2 parts ammonium phosphate, and allowing the solution to cool. Another method consists in mixing hot solutions of 7 parts disodium phosphate and 1 part of ammonium chloride:

$$Na_2HPO_4+NH_4Cl=Na(NH_4)HPO_4+NaCl.$$

The crystals obtained by this latter process contain a little sodium chloride, and must be purified by recrystallisation from hot water containing ammonia. Microcosmic salt forms transparent, monoclinic crystals of sp.gr. 1·55, which possess a saline taste and lose ammonia on exposure to air. The aqueous solution of the salt has an alkaline reaction and loses ammonia on boiling. On heating, the crystals melt easily and evolve water and ammonia, being converted into sodium dihydrogen phosphate. On further heating, more water is evolved and a residue of sodium hexametaphosphate remains as a clear, glassy mass. This substance possesses the property of dissolving many metallic oxides with formation of characteristically coloured compounds, hence microcosmic salt is largely employed in blowpipe analysis. With silica and many silicates it yields the characteristic so-called 'silica skeleton' bead.

Sodium orthophosphates of the composition $Na_3H_3(PO_4)_2$ and $NaH_5(PO_4)_2$ have also been prepared (Giran, Compt. rend. 1902, 134, 711; Senderens, *ibid.* 1902, 134, 713).

Sodium metaphosphates. A large number of these salts have been prepared. The different classes are known as mono-, di-, tri-, hexametaphosphates, &c., and are to be regarded as derived from the simple metaphosphoric acid HPO_3 and its polymers $(HPO_3)_n$.

According to Tamman (Zeitsch. physikal. Chem. 1890, 6, 122; J. pr. Chem. 1892, [ii.] 45, 417) the hexametaphosphates exist in metameric forms, and the different classes of the sodium metaphosphates are represented in the following table:—

$Na_2(PO_3)_2$	sodium dimetaphosphate
$Na_3(PO_3)_3$	„ trimetaphosphate
$Na_6(PO_3)_6$	„ hexametaphosphate
$Na_2[Na_4(PO_3)_6]$	metameric sodium hexametaphosphates
$Na_4[Na_2(PO_3)_6]$	
$Na_5[Na(PO_3)_6]$	
$NaPO_3$	Three insoluble monometaphosphates.

According to Warschauer (Zeitsch. anorg. Chem. 36, 137) the so-called dimetaphosphate is in reality a tetrametaphosphate. All the metaphosphates of sodium are soluble in water except the monometaphosphates. The tri- and tetra- salts may be distinguished from one another by the action of barium chloride or lead nitrate, the latter class giving white precipitates with these reagents. The hexametaphosphates are glassy amorphous salts, which yield precipitates with solutions of salts of the alkaline earths and heavy metals. For further details concerning the sodium metaphosphates, reference must be made to the original papers. *See* Tamman (*l.c.*), Knorre (Zeitsch. anorg. Chem. 1900, 24, 378), and Warschauer (*l.c.*), where an account of the literature on the subject is given.

Sodium pyrophosphates. Normal sodium pyrophosphate $Na_4P_2O_7$ is produced, as already stated, by heating the disodium hydrogen orthophosphate to 300°, when it remains as a white, glassy mass of sp.gr. 2·37 (Clarke), which melts at about 880°. The salt dissolves in water, yielding a solution having an alkaline reaction, and can be obtained by evaporation in monoclinic crystals of sp.gr. 1·82 containing 10 mols. of water. The aqueous solution is not converted into the orthophosphate by boiling alone, but the presence of an acid, even such a weak one as acetic acid, is sufficient to effect the change on heating.

Sodium pyrophosphate is occasionally used in medicine in place of the disodium orthophosphate, and also serves as the material for the preparation of the insoluble metallic pyrophosphates and their double salts.

Disodium hydrogen pyrophosphate

$$Na_2H_2P_2O_7$$

is prepared by heating sodium dihydrogen phosphate NaH_2PO_4 to 200° for several hours, or more easily by dissolving the normal pyrophosphate in glacial acetic acid and precipitating with alcohol. It then forms a white, crystalline powder which dissolves easily in water, giving a solution with an acid reaction. By evaporation it may be obtained crystallised with 4 or 6 mols. of water.

A delicate test for alkaline pyrophosphates is furnished by luteocobaltic chloride

$$[(NH_3)_6Co]Cl_3,$$

which gives a pale reddish-yellow precipitate with these salts. By means of this reaction $\frac{1}{750}$ part of pyrophosphate can be detected in the presence of ortho- and metaphosphate (Braun, Zeitsch. anal. Chem. 3, 468).

A considerable number of double pyrophosphates of sodium with potassium, calcium, barium, and other metals have been prepared.

Sodium carbonate (*Carbonate of soda*).

Natural occurrence of the sodium carbonates. The sodium carbonates are found in many mineral waters (especially those of Aix-la-Chapelle, Karlsbad, and Vichy), in the 'natron lakes' of Hungary, Egypt, Central Africa, the Caucasian steppes, and in those of North and South America; also as efflorescences in such steppes, especially in the neighbourhood of natron lakes. These efflorescences or crusts are formed either by the partial or entire drying up in summer of such lakes or ponds, or else by the evaporation of subsoil moisture, more moisture (containing soda) being always brought to the surface by capillary action. The soda thus obtained in various places is known by the names *natron, trona,* or *urao.* 'Urao,' according to Chatard (Bulletin No. 60, U.S. Geological Survey, 1887–1888), is essentially a carbonate of the formula $Na_2CO_3,NaHCO_3,2H_2O$, and is the most usual form of 'natural soda.'

The oldest-known occurrence of natural soda is that in Lower Egypt, where the natron lakes dry up in summer, leaving crusts of salt behind; in other places the 'trona' appears as efflorescences on the ground, consisting essentially of sodium sesquicarbonate, according to former assumptions, or rather, according to Chatard, of 'urao' mixed with other carbonates. Several thousands of tons of this article are yearly exported from Alexandria, principally for soapmaking. Enormous quantities of soda are found in the lakes and steppes of the 'Alkali Plain' and other parts of the great desert east and west of the Rocky Mountains. One of the most considerable of these occurrences is in Owen's Lake, in California, which, according to Chatard, contains per litre:

26·96	grms.	Na_2CO_3
5·71	„	$NaHCO_3$
11·08	„	Na_2SO_4
29·41	„	NaCl
3·14	„	KCl

with a little silica, alumina, calcium, magnesium, and boric acid. This lake contains from twenty to forty millions of tons of sodium carbonate, which is easily obtained in an almost pure state by solar evaporation in shallow ponds. The Magadi deposit in British East Africa, which is about 30 square miles in area, is estimated to contain some 200,000,000 tons of soda. The following analysis is by A. Gordon Salamon:—

Na_2CO_3	43·55
$NaHCO_3$	40·41
NaCl	0·36
SiO_2	0·07
$Al_2O_3+Fe_2O_3$	0·04
Water (by diff.)	15·57
	100·00

Magadi, which in the native dialect denotes 'soda,' is situated about 370 miles from the port of Mombasa, and some 60 miles to the south of Nairobi. The deposit of natural soda is located at about 2000 ft. above the level of the sea, and lies in a deep depression called the Rift Valley, at some 3000 ft. below the level of the Central African plateau that surrounds it.

This natural soda is a crystalline sodium sesqui-carbonate which, when calcined, at a low red heat, yields sodium carbonate (soda ash) in powder form, of 99 p.c. purity. The density of Magadi soda ash will correspond to what is known as 'heavy' finish (*v.* p. 69), which is an important point in its favour, both for considerations of sale, as well as cheap cost of transport.

The development of this natural soda deposit has been undertaken by the Magadi Soda Company, Ltd., formed in 1911 with a capital of £1,312,500. A branch line of about 92 miles is being constructed from the Uganda railway to Magadi, and a deep-water pier and sidings are in the course of construction at Mombasa, thereby establishing through railway communication between Magadi and the sea, and ships will be able to lie alongside this pier when taking in cargoes of soda. It is expected that a start will be made with the exportation of soda in the early part of 1914.

Mombasa, being, so to speak, half way to the Far East, is well situated for supplying such important markets as Japan, China, and Australia; it is also in immediate proximity to the markets of India and Cape Colony.

Soda from the ashes of plants. Whilst the soluble part of the ashes of most land plants contains chiefly potassium carbonate and other potassium salts, there exist some 'soda plants,' growing on the sea-shore or near salt-springs, the ashes of which furnish a very impure kind of soda, formerly much used by soap-makers. Most of these plants belong to the family *Atripliceæ*—namely, the genera *Atriplex, Chenopodium, Salsola, Salicornia, Kochia,* &c. The plants growing in the sea itself, especially *fuci*, yield another kind of ashes, called 'kelp' in Scotland and 'varec' in Normandy, contain very little sodium carbonate, but a large quantity of potassium chloride and sulphate, along with a little iodate, which formerly was the only available source of iodine; in its manufacture, 'kelp salt'—that is, sodium chloride containing some carbonate—was obtained as a by-product. The ashes from the real soda plants growing in Spain are known in commerce as 'barilla'; those from the south of France as 'blanquette,' 'salicor,' 'soude douce,' &c. The general name of these products is *vegetable soda*, but frequently *barilla* is used in the same sense.

Vegetable soda, being simply fluxed ashes not purified by lixiviation, contains a large proportion of residue insoluble in water; the portion soluble in water contains sodium and potassium carbonate, sulphate, and chloride, along with small quantities of sulphides and thiosulphates formed by reduction from the sulphates; it is, moreover, frequently adulterated with a large quantity of common salt. In the analyses by Girardin, the proportion of sodium carbonate varies from 2 to 13·76 p.c. (Lunge, Sulphuric Acid and Alkali, Vol. II., pt. i., p. 81.

Artificial soda.

Historical. Only when Duhamel, in 1736, had demonstrated the identity of the base of common salt with that of 'mineral alkali,' as the natural soda was then called, was it possible to think of manufacturing soda artificially. But the problem was not actually approached until about 1775, when Scheele discovered that common salt could be partially converted into caustic soda by means of lead oxide. In the same year the French Academy of Science offered a prize for a method of converting common salt into soda; and this was a stimulus to many inventors, only one of whom, Nicolas Leblanc, ultimately proved successful. His first experiments are said to have been made as far back as 1784; in 1789 his process was so far completed that he was able to submit it to the Duke of Orleans (whose domestic physician he was) in order to obtain the capital for carrying it out on a manufacturing scale. This led to several agreements in 1790, and, in 1791, to a patent which practically embodies all the principles of the Leblanc process as carried out to-day. About the same time manufacturing operations were commenced at La Franciade, at St. Denis. Leblanc himself did not profit by his invention, as his patent was taken from him by the French Revolutionary Government 'for the benefit of his country,' and ultimately the unfortunate inventor of what has proved one of the greatest industrial processes of modern times committed suicide in despair.[1]

Even before Leblanc fell a victim to the ingratitude of his countrymen, several alkali works employing his invention were founded in France. In England the first attempts at manufacturing artificial soda were made by W. S. Losh, at Walker, near Newcastle-on-Tyne, in 1806; the Leblanc process was tried there on a very small scale in 1814, and at St. Rollox in 1818. The enormous salt duty levied in England (30*l.* per ton) at that time practically prevented the establishment of alkali works. Immediately after its abolition in 1823 James Muspratt started his works near Liverpool, which for 6 years remained the only one in England, except a few small works on the Tyne. The small quantity of black ash then made in France and England contained only about 10 or 12 p.c. of alkali; Muspratt, however, from the first succeeded in making it of a strength of 24 p.c. of alkali, and in this form it was sold to the Liverpool soap makers to be used in lieu of kelp.[2] It was found when this black ash was exported that it quickly lost strength, and this led to the manufacture of sodium carbonate by lixiviation, evaporation of the liquor, and calcination of the residue.

During the ensuing 50 years an enormous development of the production of sodium carbonate, and later of caustic soda, by the Leblanc process took place in Great Britain and on the Continent, and during this period the Leblanc process was practically without a rival. Although the Leblanc process still fully maintains its position for the manufacture of caustic soda, it has been practically superseded by the ammonia soda process for the production of sodium carbonate,

Later still, electrolytic processes have been evolved and worked on a commercial scale. The various natural deposits of soda existing in different parts of the world have up to now played a small part in the soda industry.

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[1] Report of the Committee of the French Academy May 31, 1856, and especially 'Nicolas Leblanc,' par Aug. Anastasi, Paris, 1884.

[2] E. K. Muspratt, J. Soc. Chem. Ind. 1886, 408.

GENERAL REMARKS ON THE MANUFACTURE OF SODA.

The only raw material, offered by nature in inexhaustible abundance for the manufacture of both sodium and chlorine compounds, is sodium chloride, which, as rock-salt, forms whole geological strata, and which can be obtained very cheaply as rock-salt, or by evaporation from brine, or in sunny climates from sea-water by the sun's heat. All other raw materials are of very little importance for that purpose; those which possibly contain as abundant a supply of sodium—namely, soda-felspar and certain other silicates—are not fit for the economical extraction of soda. As a source of chlorine, the magnesium chloride, produced in enormous quantities as a by-product of the Stassfurt potash industry, has been regarded as a possible rival of sodium chloride, but is, in any case, only indirectly concerned in this question, in so far as it may influence the economical aspects of the various soda processes.

The object of the alkali manufacturer is to decompose sodium chloride according to the following equation:

$$NaCl + H_2O = NaOH + HCl.$$

Thermo-chemistry, however, shows this reaction to be endothermic.

$$\underbrace{\overset{[Na{\cdot}Cl]}{97{\cdot}7} + \overset{[H_2{\cdot}O]}{58{\cdot}0}}_{155{\cdot}7} = \underbrace{\overset{[Na{\cdot}OH]}{102{\cdot}3} + \overset{[H{\cdot}Cl]}{22{\cdot}0}}_{124{\cdot}3}$$

As a rule, chemical change can only take place if the thermal units represented by the formation of the new compound or compounds are superior to those of the original compound or compounds. In order to bring about changes of an inverse order, such as that which concerns us here, we have practically only two means at our command: either the employment of a physical force more potent than heat in overcoming the latent chemical energy—that is, electricity—or else, turning the difficulty by first applying some intermediate reaction which converts the original compound into one more easily split up by chemical means, aided by a proper temperature. This necessitates the employment of auxiliary substances, which sometimes are and sometimes are not recovered in the later stages of the process; sometimes new products are formed which contain one of the constituents, either of the original substance or of the auxiliary bodies in such a form that it seems, and frequently for a time actually is, economically impossible to recover the same.

1. THE MANUFACTURE OF SODA BY THE LEBLANC PROCESS.

This process consists in first of all converting the sodium chloride into sodium sulphate (*see Salt-cake*, p. 21), and then in heating the sodium sulphate with calcium carbonate and coal until the mass has fluxed. No reaction takes place until the mixture has become a semi-fluid, pasty mass, after which the reaction is rapid and practically complete.

The fluxed mass so obtained is called 'black ash,' and the batches drawn out of the furnace are frequently called 'balls.' Black ash is a very complex mixture of substances, which undergo a somewhat rapid change by the action of the air. It is separated by the action of water ('lixiviation') into a residue—'tank waste,' 'alkali waste,' or 'soda waste'—and a solution containing the soda chiefly in the state of carbonate, along with some hydroxide and a large number of impurities. From this either the commercial sodium carbonate ('soda ash') or the commercial hydroxide ('caustic soda') is prepared by operations to be described below.

The reaction taking place in the black-ash furnace has been variously interpreted. The matter is complicated, not merely by the large number of substances found in black ash, but also by the fact that, in order to fully decompose the sodium sulphate, an excess of calcium carbonate and coal must be employed. Taking an average of the many mixtures employed in practice, we may assume that with 100 parts of pure Na_2SO_4 usually about 100 parts of pure $CaCO_3$ and 35 of pure C are employed—that is, to 1 molecule of Na_2SO_4 1·42 mols. of $CaCO_3$ and $4\frac{1}{8}$ mols. of C; or, say, $1\frac{1}{2}$ of $CaCO_3$ and $4\frac{1}{8}$ of C; and the older theories, in fact, assumed those proportions to represent the number of molecules entering into the reaction, without taking into account the fact that in a case like the black-ash process, where the mixture never enters into complete fusion and the ingredients are never absolutely mixed with one another, the decomposition of the most valuable portion, the Na_2SO_4, can be brought about only by a mechanical *excess* of the other ingredients, which ensures that every portion of the Na_2SO_4 comes into contact with them.

Apart from this oversight, the first theory of the black-ash process—that of Dumas (1830)—was based on two erroneous assumptions, namely, that CaS is soluble in water (confounding the compound $Ca(SH)_2$ with CaS, as was natural at that time); and that there exists in black ash an insoluble calcium oxysulphide 2CaS,CaO (already assumed by Thénard). Believing that the action of water must cause CaS at once to act upon Na_2CO_3, Dumas thought that this is prevented by the formation of 2CaS,CaO, and he represented the black-ash process in this way:

$$2Na_2SO_4 + 3CaCO_3 + 9C = 2Na_2CO_3 + CaO,2CaS + 10CO.$$

This would require for 100 Na_2SO_4 : 105·6 $CaCO_3$, and 38 pure C—quantities decidedly in excess of those found sufficient at many alkali works for *completely* decomposing the salt-cake, which fact alone would refute Dumas's theory.

That theory was further, but not very essentially, modified by Unger, Brown, P. W. Hofmann, and E. Kopp, and was almost universally adopted until Kynaston Gossage, and Scheurer-Kestner (1858–1867) exposed its fallacy by proving the non-existence of calcium oxysulphide in black ash, and by other reasons equally cogent. They also disputed the assumption that the principal oxide of carbon formed is CO, not CO_2—a theory upheld by Dubrunfaut, and later on by Mactear, but refuted by the extensive investigations of Kolb (Ann. Chim. Phys. [iv.] 7, 118), and by laboratory experiments made by Lunge and Fischer.[1]

As the final result of the prolonged controversy on these points, of the large-scale experiments of Scheurer-Kestner and Kolb, and of

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[1] Compare the complete discussion of the various publications on the theory of the black-ash process in Lunge's Alkali, vol. ii. pt. ii. p. 511.

Lunge, the theory of the black-ash process may be stated as follows: the principal reaction going on is ultimately

$$Na_2SO_4+CaCO_3+2C=Na_2CO_3+CaS+2CO_2.$$

It is, however, extremely probable that this takes place in two stages, the first being the reduction of sodium sulphate by carbon to sulphide; the second being a mutual decomposition of the latter with calcium carbonate:

$$(1)\ Na_2SO_4+2C=2CO_2+Na_2S.$$
$$(2)\ Na_2S+CaCO_3=Na_2CO_3+CaS.$$

Nearly all the Na_2S is at once acted upon by $CaCO_3$ immediately after its formation, so that there is at no time any considerable proportion of it present, except in the case of abnormal work.

The above equations would require for 100 parts of pure Na_2SO_4 only 70·42 pure $CaCO_3$ and 16·9 pure C. One reason why much more of the two last ingredients must be employed for decomposing the whole of the Na_2SO_4 has been already stated, but there is an additional reason. In order to lixiviate the melted mass, it must have a certain degree of porosity, and must, moreover, be further disintegrated during the treatment with water. Without this, the lixiviation would require too much time, too high a temperature, and too great dilution of the liquor, and would thus produce a very inferior liquor, as well as a bad yield of soda. The above condition is practically attained by employing an excess of limestone and coal, which in the last stage of the process, when the temperature is at its highest, react as follows:

$$CaCO_3+C=CaO+2CO.$$

The carbon monoxide, which is formed at a period when the mass has become pasty, causes it to become honeycombed, like the dough in a fermenting loaf of bread. The CO is actually seen escaping at this stage, and burning with a flame tinged yellow by sodium. The caustic lime remains behind, and afterwards, on being hydrated, causes the balls to swell up and burst during the lixiviation. A further excess of limestone and coal, which ought not to be too great, produces greater porosity of the black ash in a purely mechanical way, since they are not fused like the remainder of the mass. Lastly, some portion of the coal is unavoidably burned before it can enter into action. All these reasons fully explain the necessity of employing an excess of limestone and coal; but it is impossible to embody this in a chemical formula, as has been attempted by Scheurer-Kestner, seeing that such excess acts merely in a mechanical way, and actually differs in different works.

It is hardly necessary to say that many subsidiary reactions take place at the same time; but these have nothing to do with the theory of the black-ash process, and merely explain the occurrence of the impurities always found accompanying the two principal products, sodium carbonate and calcium sulphide.

DESCRIPTION OF THE BLACK-ASH PROCESS.

Raw Materials.

Sodium sulphate (*salt-cake*). This is nearly always obtained by the decomposition of common salt by sulphuric acid, or else by Hargreaves and Robinson's direct process from common salt, pyrites kiln gases, and air (*cf. Sodium sulphate*).

The salt-cake for alkali-making should be a white or yellowish powder containing only porous, friable lumps, and no fluxed pieces which nearly always inclose some raw salt and decompose badly in the black-ash furnace.

Good, strong soda cannot be made with salt-cake containing more than 0·5 p.c. of undecomposed NaCl.

Good commercial salt-cake contains 96–97 p.c. of Na_2SO_4.

Calcium carbonate. Both limestone and chalk are employed—of course, the purer the better. Magnesian limestone cannot be used, and limestone or chalk containing much silica causes a great loss of soda in the insoluble state. The chalk ought to be dried, and both it and the limestone ought to be crushed to about 2-in. cubes.

The Tyneside works mostly use the chalk brought down from the Medway by colliers as ballast. The Lancashire works employ mostly Buxton limestone, which works more easily in the furnaces than does chalk, and requires less heat for the 'balling' process.

In most cases the lime mud obtained in causticising the liquors by lime is used to replace part of the limestone in the black-ash mixture.

Coal. The quality of the coal employed for the black-ash mixture is of great importance. It ought to contain as little ash as possible. and this is more difficult with the small coal or 'slack' generally used than with lump coal, which is, however, too dear for this purpose. Even after washing, such small coal rarely contains less than 5 p.c. of ash; 6 p.c. is the maximum tolerated by some German alkali works; but in England 'slack' containing 8 p.c. ash is considered as very good for mixing. The coal ashes, consisting principally of aluminium and calcium silicates and ferric oxide, cause the formation of insoluble double silicates, which lock up a considerable portion of soda in a non-available form. The more ashes the mixing-coal contains, the less soda ash will be obtained with it.

Leblanc himself employed wood charcoal, which is now excluded by its price. Good lignite or crushed coke, if otherwise pure, can be very well employed in mixing. In any case care must be taken to decide by preliminary trials on a working scale whether a certain description of coal will answer for soda-making or not, as the whole success of the operation depends upon this, and analyses cannot entirely decide this point beforehand.

The nitrogen contained in coal, which varies from 0·5 to 0·75 p.c., gives rise to the formation of cyanides, part of which are converted into cyanate by the oxidising action of the flame. The moisture of the air decomposes the cyanate, with formation of ammonia, which is evolved during the cooling of the balls. But another portion of the cyanide remains behind, and is, during the lixiviation, converted into ferrocyanide.

J. Pattinson (in Trans. Newcastle Chem. Soc. 4, 183) gives analyses of nine descriptions of mixing-coal as used on the Tyne. That described as 'good' contains, in 100 parts, 61·19–66·45 fixed carbon, 25·27–27·35 bituminous substances, 0·6–1·47 volatile sulphur, 0·1–0·3 sulphur in ashes, 4·8–8·32 ashes, and 1·01–

1·67 moisture. 'Inferior' mixing-coal contains only 56–58·8 fixed carbon, and 12·56–14·22 ashes.

Mixing-coal acts all the better the more finely divided it is; it is, however, rarely ground by itself, especially as it is mostly employed in the state of 'small' or 'slack,' but is only screened and roughly mixed with the other materials.

The proportions in which the materials are mixed naturally vary with their quality, the amount of moisture, &c. Leblanc's original proportions: 100 salt-cake, 100 chalk, 50 charcoal, are very nearly identical with those now in use.

THE BLACK-ASH FURNACES.

The furnace in which the Leblanc process was originally worked was naturally a hand furnace. Hand furnaces are now no longer used for the production of black ash, but as a matter of historical interest, the following illustrations (Figs. 31, 32, and 33) and description are added. The furnaces were substantially built and well-braced, and the position of the working doors and shape of the furnace allowed easy access for the working tools to all parts of the beds.

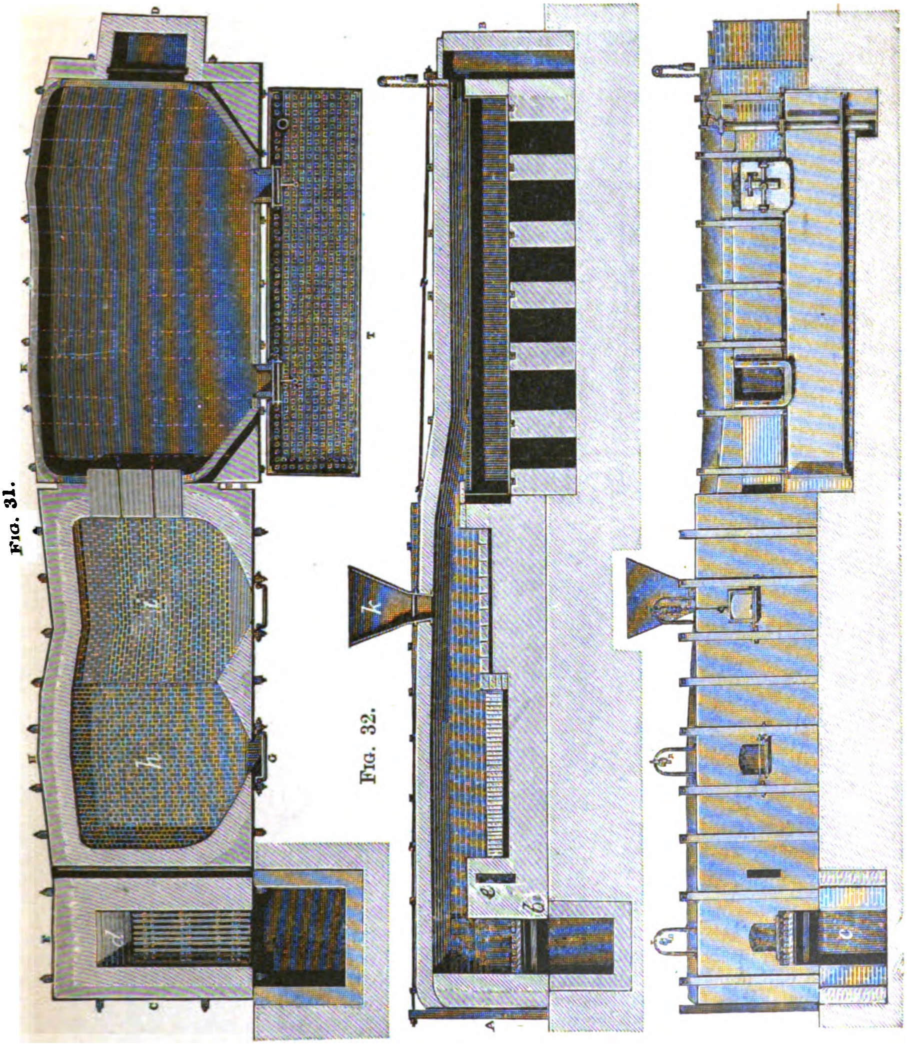

FIG. 31.

FIG. 32.

FIG. 33.

Fig. 31 is a sectional plan along line A B of Fig. 32, passing through the hollow fire-bridge, but showing the beds and the pan from the top; Fig. 32 is a sectional elevation along line C D of the plan; Fig. 33 a front elevation, showing only the firing hole and the drainer in section. Such a furnace worked off a 3-cwt. charge of salt-cake in 45–50 mins., so that with the necessary pauses for cleaning the fire, &c., 24–27 balls were made daily. *a* is the fireplace, provided with wrought-iron grate-bars; the bar *b* assists in poking up the fire from below from the fire-cave *c*. (Such 'cave-fires' were said to consume less coals than fireplaces with their ash-pits at the level of the floor, by the greater facility they offer for attending to the fire.) At *d* the fireplace is stepped backwards, so that the flame ranges all over the bridge *e*. The latter was very carefully and strongly built of the best fire-bricks procurable, and lasted about 3 months. It was 2½–3½ ft. wide, and usually built hollow. A cast-iron bridge plate, 1½–2 ins. thick, prevented the charge from fluxing through the bridge; it was protected against overheating by an air channel, open at each end. *h* and *i* are the two furnace-beds. The charge was put through a hopper *k* or else through the door, on the back bed *i*, which was 3 ins. higher than the front bed *h*; to this the charge was transferred, when it was empty, in order to be finished and drawn out through its door. Sometimes three-bedded furnaces were met with. The front bed *h* was made of bricks on end, and was set upon a layer of ground chalk or fireclay, to isolate it from the foundation. The bricks were set dry, as closely together as possible (preferably grinding them upon one another, so as to minimise the width of the joints), and were grouted on the top with a thin paste of fireclay. The long joints were made to run towards the door, and the whole bed was made to slope about 2 ins. that way, in order to facilitate the working of the tools. The back bed *i* was made of bricks on edge (*i.e.* 4½ ins. high). The diagrams show how these beds were made within fire-brick 9-in. walls, so shaped that the tools could easily reach every part of the beds, and leave no dead corners. The front or working-bed, even if made of the best material and with the greatest care, rarely lasted longer than 5 months.

On the Tyne the furnaces were cased in solid cast-iron plates, tied together by upright binders and tie-rods; but in Lancashire the plates were frequently replaced by the less substantial plan of simple straps of wrought iron, 3-6 ins. broad and ¾ in. thick. The ends of the tie-rods were tightened up by screws and nuts, or else by loops and wedges.

In front of the working-doors there were special door plates and supporting bars for the tools. The doors were best closed by fire-clay slabs, surrounded by an iron frame, and hung from a standard with chain, pulley, and balance-weight.

These hand furnaces, like the early mechanical black-ash furnaces, were erected for the manufacture of sodium carbonate, and were fitted with pans over which the fire gases leaving the furnace passed on their way to the chimney, and in which they concentrated by top heat the crude sodium carbonate solution obtained on lixiviation of the black ash. Figs. 31, 32, and 33 show the concentrating-pan, the working of which is described later under the mechanical black-ash furnace or revolver (p. 41).

The work in the black-ash furnace was carried on as follows: The mixture was put on the back bed, where it was levelled, and during its stay there was twice turned over, in order to dry it and heat it. When the charge in the front bed had been drawn out the fire was allowed to play on the empty bed for a little while to make it hot, and then the previously heated charge was pushed over from the back bed. Sometimes a portion of the ball was left a little longer on the back bed ('splitting a ball'). As soon as it was empty a fresh charge was put in. The principal work, of course, went on on the front bed, which was heated to at least the melting-point of silver.

Revolving black-ash furnaces. The kind of work done by a ball-furnace can be done more efficiently and cheaply by mechanical means, as it simply consists in keeping the charge turned over. The actual solution of this problem proved, however, a difficult task, even after the right principle, that of a cylindrical furnace revolving as a whole, had been found by Elliott and Russell, in 1853. Apart from the mechanical imperfections of their furnace, it turned out the black ash much too hard and in a very bad state for dissolving, because by the continuous rotation all the gas was driven out, and the honeycombed structure of the balls was lost. Stevenson and Williamson, in 1855, overcame both difficulties, and must be called the true originators of mechanical black-ash furnaces, usually called 'revolvers,' which have entirely superseded the hand furnaces.

Figs. 34 and 35 show an ordinary revolving black-ash furnace in sectional plan and in elevation, fitted with the top-heat pans employed to utilise the waste heat from the revolver when ash or sodium carbonate is produced from the liquors.

Fig. 36 represents a revolver fitted in accordance with the custom to-day with bottom-heated pans to utilise the waste heat.

Where black ash, as is practically always the case now, is made to manufacture caustic soda, these pans are used to concentrate the weak caustic soda solution obtained from the causticisers. It is obvious that it would be impossible to pass the fuel gases over the causticised liquor without carbonating it, and hence the less efficient bottom heating has to be adopted. *a* is the fireplace, with two working doors and a cylindrical opening, 2¾ ft. wide, for the flame to pass through. Between this and the revolving cylinder there is a fire-brick lined, cast-iron ring *b*, the 'eye,' hung by means of chain and pulleys, which allows some air to enter all round, and the necessary expansion to take place. The cylinder *c* consists of a shell of ½-in. boiler plates, 15½ ft. long and 10½ ft. wide inside; cast-iron tire seats *f f*, and cast-steel tires *g g*, are shrunk upon the barrel, and work upon the V-rollers *h h*. The cylinder is lined inside with fire-bricks, 9 ins. thick in the centre, 1½ ft. at the ends; this facilitates the running out of the charge. Two horizontal 'breakers' project from 9 to 13 ins. above the other lining, and promote the mixing of the charge in revolving. A 1½-ft. manhole closed by an iron lid allows charging and emptying the furnace. Each furnace is provided with a special engine, possessing double gearing so that it can produce either a slow movement (one revolution in 10 mins.) or a quick movement (five revolutions per minute). The gearing acts upon a spur-wheel *m*, made in one piece and bolted immovably to the furnace. The exit opening *l* communicates with the large dust chamber *m'*, to which are joined the two boiling-down pans *n* and *n'*, 28 ft. long by 8 ft. wide by 2¾ ft. deep each, with their drainers *o* and *o'*, and from these the flame goes through the flues *q q* into a chimney. The purpose of the partition *r* in the pans is to reserve one part for evaporating the mother-liquor pumped up from the drainers.

A tramway runs above the furnaces for charging them, and another (smaller) tramway runs underneath them for moving the train of discharging trolleys or bogies into which the finished charge is run from the revolver.

A furnace of this size takes charges of 30 cwts. salt-cake and gets through 15–18 tons of salt-cake in 24 hours, with a consumption of 10–13 cwts. of firing fuel per ton of salt-cake.

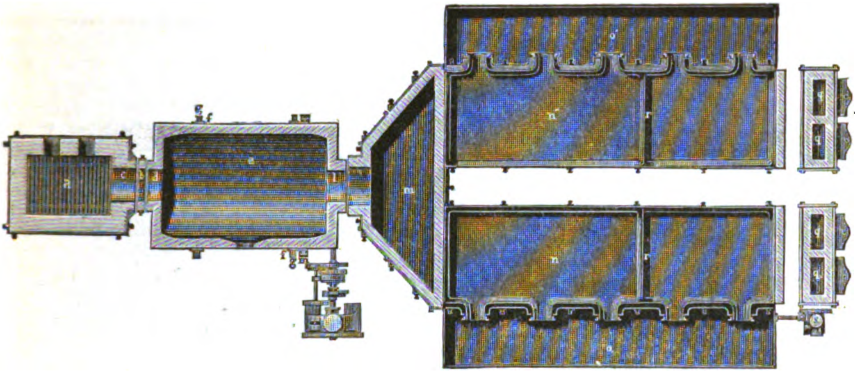

FIG. 34.

Much larger revolvers have been erected, a common size being 18 ft. in length by 10 or 12 diameter. Such a revolver will decompose a 3- or 4-ton charge of salt-cake in 2 hours. The largest revolver made is one erected by the Widnes Alkali Co., in 1887; it is 30 ft. long and 12 ft. 6 in. in diameter (described by Watson Smith in the J. Soc. Chem. Ind. 1887, 417), and decomposes a charge of 8 tons 12 cwts. salt-cake in 3½ hours; and one at the works of Messrs. Kurtz, St. Helens, which is 30 ft. 6 ins. long and 12 ft. 6 ins. diameter.

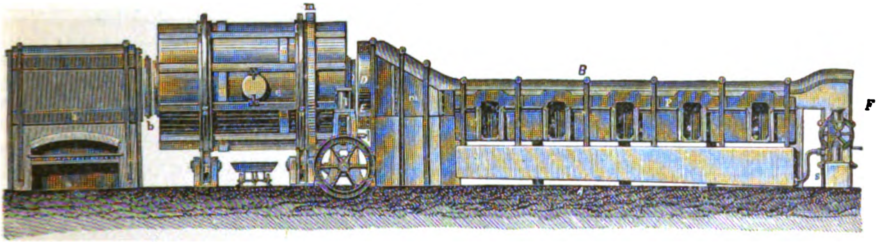

FIG. 35.

There has been much controversy as to the best way to mix and work the charge in a 'revolver.' The various methods suggested had for their object: (1st) The production of a more porous and more easily lixiviated black ash, and (2nd) the destruction of the cyanides formed in the ordinary process which are responsible for carrying iron forward in a soluble form to the end of the process.

The following methods of working the charge have been practised:—

1. The chalk or limestone and two-thirds of the coal are introduced and the revolver kept slowly turning round till the appearance of a blue flame of CO round the man-hole shows some caustic lime has been formed. This liming process lasts 1–1½ hours. Then the salt-cake, together with the remainder of the coal, is added and the rotation slowly continued until the mass is nearly fused, when the quick movement is started.

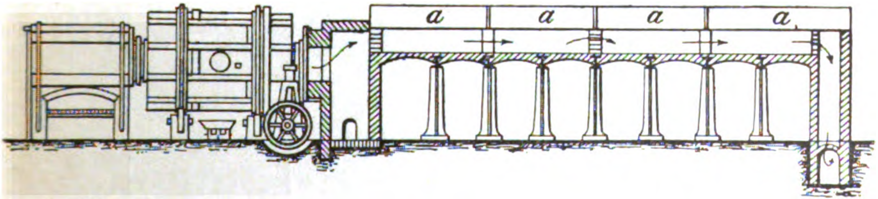

FIG. 36.

The object of 'liming' is to produce a certain proportion of caustic lime, which in the lixiviating tank will cause the balls to burst, and to be more easily dissolved.

2. Mactear in 1874 patented the following method of work. He charges the salt-cake, coal, and limestone at once, but only uses the theoretical quantity of limestone; when the charge is fused he stops the revolver and adds quicklime equal to 10 p.c. on the weight of the salt-cake, and 15 p.c. of cinders.

3. Péchiney (patents 1877 and 1878) added at the end of the charge some salt-cake which has the effect of destroying the cyanide present, and of preventing the formation of ferrocyanide.

4. Weldon patented (1878) an improvement on the Péchiney process. He added a little limestone dust to the charge along with the salt-cake suggested by Péchiney.

The advantages of the Weldon-Péchiney process were the subject of a long controversy between Weldon and Mactear.

5. Several other patents were taken out about the same time, 1878, for destroying the cyanides and ferrocyanides by Mactear, Gaskell, Deacon & Co., Pauli, Brunner, Allhusen, and Glover.

None of these processes appears to be necessary, and the present practice is to drop the whole charge into the revolver at once and work it through without stoppage or addition.

The following may be taken as the normal mixing for a black-ash revolver under modern conditions.

(*a*) When all the calcium carbonate is added as limestone; (*b*) when part of the limestone is replaced by the calcium carbonate produced in the causticisers (caustic lime mud).

	a cwt.	*b* cwt.
Salt-cake	55	52
Limestone	56	37
Lime mud	—	45
Slack	22	21

Properties of black ash. The yield of black ash is about 1¾ times the weight of the salt-cake furnaced. Properly made, black ash has a blackish-brown, in some places a liver-brown, surface; on breaking, it exhibits a slate-grey colour and porous, almost pumice-like, structure, and looks homogeneous, without any black or white streaks or lumps. Balls which are quite black on the outside are made with too much coal, or are very badly wrought, so that the mixing coal was not all consumed and the ball could not be 'cleared.' If there was a deficiency of limestone, or if the balls were overheated, they are very dense, with pale pink spots outside, and on breaking their colour is pink or purple, in the worst case brick-red. Such black ash contains very much sodium sulphide or even polysulphide. Kolb found this to occur whenever the melting-point of silver was exceeded. 'Soft' balls occur when the temperature has not been high enough, so that the mass never got beyond the thinner state to the pasty, porous one. Such black ash is very difficult to lixiviate, and contains much undecomposed sulphate.

In order to check the furnace men, samples are taken from each man's work, sometimes even from every single ball, and are roughly tested for their percentage of alkali, of sulphate, and of sulphide; but as these cannot be average samples, the judgment of a practised eye on the appearance of the ball in general must always be taken into account as well. The testing-methods are the same as those used for tank liquor (*v. infra*).

Of the published analyses of black ash many are not trustworthy, because they were evidently made with a material changed by exposure to air, or because they neglect constituents which must have been present; some of them also because they give highly detailed figures for constituents for which no good analytical methods are (or were then) known. We quote only a few:—

—	From Liverpool (Kynaston)	From Jarrow (Stohmann)		From Amiens (Kolb)
		Hand made	Revolver ash	
	a	*b*	*c*	*d*
Sodium carbonate . .	36·88	44·41	43·27	44·79
„ silicate . .	1·18	—	—	1·52
„ aluminate . .	0·69	—	—	1·44
„ sulphate . .	0·39	1·54	1·06	0·92
„ chloride . .	2·53	1·42	1·48	1·85
Calcium oxide . .	9·27	10·44	7·13	9·68
„ sulphide . .	28·68	28·87	27·73	29·96
„ carbonate . .	3·31	3·20	7·52	5·92
„ sulphite, &c. .	3·78	—	—	—
Magnesium oxide . .	0·25	0·10	0·19	—
Silica	—	0·89	1·74	—
Ferric oxide	2·66	1·75	1·48	1·21
Alumina	1·13	0·79	0·72	—
Iron sulphate	0·37	—	—	—
Ultramarine	0·96	—	—	—
Sand	0·90	2·20	2·66	—
Coal	7·01	5·32	5·28	1·20
Water	0·22	—	—	—
Total . . .	100·21	100·93	100·26	98·49

These analyses do not show caustic soda, which is, in fact, only formed on lixiviation; neither do they count up a number of rare substances, found by some authors in the samples examined by them. But the analysts ought not to have neglected the cyanide, nor the soda present in an insoluble form. There is also no mention of Na_2S, which is never quite absent. All these are accounted for in the following partial analyses of black ash made by the Péchiney-Weldon process:—

—	Made with 60 per cent. coal on the sulphate	100 sulphate, 77·8 limestone, 36·1 coal.	100 sulphate, 85·3 limestone, 44·1 coal
Alkali	22·60—24·51	24·25—26·00	23·00—26·25
Na_2S	0·28— 0·38	0·31— 0·48	0·20— 0·37
Na_2S to 100 alkali	1·15— 1·60	—	—
Na_2SO_4	0·41— 0·63	0·18— 0·90	0·18— 0·90
Total Na_2SO_4 after oxidation	1·85— 2·24	0·88— 1·90	0·96— 2·00
Available alkali in soda ash	57·40—58·30	—	—
Alkali in soda waste	0·21— 0·37	0·19— 0·23	0·17— 0·32
Na_4FeCy_6	—	traces—0·06	traces—0·052

Jurisch (J. Soc. Chem. Ind. 1880, 241) gives the following analyses (in which we abridge the three decimals of the percentages to one):—

—	Muspratt, revolver, July 1874	Muspratt, hand, November 1874	St. Rollox, Mactear's revolver process. Feb. 1886	Muspratt, Mactear's revolver process, April 1886
Mixture: Salt-cake	100	100	100	100
Limestone	106	109	73	78
Coal 10 p.c. ash	55	56	41	47½
Mactear's lime	—	—	7	7½
Na_2CO_3	41·6	41·8	45·3	46·2
NaCl	1·2	1·4	1·7	0·7
Na_2SO_4	1·2	2·3	1·5	0·4
Na_2SO_3	0·14	0·5	—	—
$Na_2S_2O_3$	—	0·3	1·3	0·6
SiO_2	2·4	3·1	3·1	2·7
Al_2O_3	1·1	1·5	1·0	0·8
Fe_2O_3	0·9	1·1	0·7	1·0
$CaCO_3$	11·6	6·6	5·1	9·7
CaO	5·7	5·8	1·3	1·7
CaS	29·8	31·9	31·0	33·6
MgO	—	0·3	0·3	0·4
Coke	4·4	3·3	7·4	3·5

Black ash keeps unchanged in the absence of moisture and carbon dioxide, but in the presence of these it soon undergoes a change (studied by Kolb, Ann. Chim. Phys. [iv.] 7, 118; 8, 135; 10, 106). The lime attracts both H_2O and CO_2; on being hydrated it swells up and cracks the balls, which gradually fall to powder. On lixiviating, they now yield less NaOH, but, on the other hand, much more Na_2S and products of its oxidation, since the action of the atmosphere on CaS produces calcium hydrosulphide, polysulphide, thiosulphate, and other soluble calcium compounds which, on lixiviation, at once react on sodium carbonate. In the course of time the reaction may thus be reversed, and the sodium carbonate may be entirely decomposed again. Hence black ash ought not to be kept too long before working it up, and ought not to be exposed to the action of the air after being once cooled down.

The action of *water* on black ash has also been studied by Kolb (*l.c.*). From his experiments he draws the following conclusions. The quantity of NaOH formed in the lixiviation vats, by the action of lime on sodium carbonate, is not materially influenced by the quantity of water, but increases both with the time of digestion and the rise of temperature. Almost exactly the same conditions govern the formation of sodium sulphide, but this is independent of that of caustic, and evidently takes place by the action of dissolved CaS on Na_2CO_3. NaCl slightly increases, Na_2SO_4 slightly diminishes the quantity of CaS entering in solution, which always takes place in the shape of $Ca(SH)_2$. Boiling CaS with water will effect this slowly. Solutions of Na_2CO_3 act all the more on CaS the more dilute and the hotter they are, and the longer they remain in contact with each other; the presence of caustic lime or caustic soda retards this action. Hence the lixiviation should be carried on as quickly and at as low a temperature, and with as little water, as possible.

Lixiviation of Black Ash.

During the first period of the manufacture of artificial soda, the black ash, as it came out of the furnace, was directly sent out to soap makers and other consumers. Usually (in England universally) the black ash is separated by *lixiviation* into a soluble and an insoluble portion. The former yields commercial soda ash, crystals or caustic; the latter, which contains CaS, as well as many impurities, was a waste product, until quite recently very imperfectly, if at all, utilised.

The lixiviation is not merely a mechanical process for dissolving the soluble matter; during its course chemical reactions set in, which are partly comparatively harmless (as the formation of some $NaOH$), but some of which may cause very much loss by the conversion of Na_2CO_3 into Na_2S, Na_2SO_4, and intermediate states of oxidation, as will be understood from the remarks made upon the action of water on black ash.

Properly made porous black ash requires only breaking up into large pieces, so that it can be handled; but dense, overheated or underheated black ash must be crushed to a coarse powder, and even then is nothing like completely exhausted, without reconverting much of it to Na_2S. It is, of course, essential that black ash should be completely exhausted, that the liquor should be pure, and that it should be as concentrated as possible. We have seen above that this can be done only by working quickly and at a moderate temperature. The latter is specially required for weak liquor, which is much more liable to act upon CaS than concentrated liquor. The former should never be hotter than 43°, and is much better kept between 32° and 37°; the latter may reach 60°.

It is further necessary to disturb the solid mass as little as possible, in order to prevent the liquor from becoming muddy; and, more particularly, any exposure of the wet solid residue to the atmosphere must be avoided, because this leads to a rapid oxidation of CaS, even as far as $CaSO_4$, and a consequent loss of soda.

The different apparatus formerly used for lixiviating soda ash need not be described here, as they are completely obsolete. The apparatus universally employed was originally invented by Professor Buff, of Giessen, but was apparently first brought into practice by Dunlop, at St. Rollox, in 1843, and made its way, first into Lancashire (about 1860). In England it seems to have been dominant about 1864, on the Continent 10 years later. Its principle is to allow the black ash to remain in the same place, and to cause the liquor to circulate in a methodical manner, so that it is brought up to concentration, and the black ash is completely exhausted at the same time, without ever being exposed to the air. By this course the liquors are much stronger and purer, and the process is much less expensive than with the plans formerly practised.

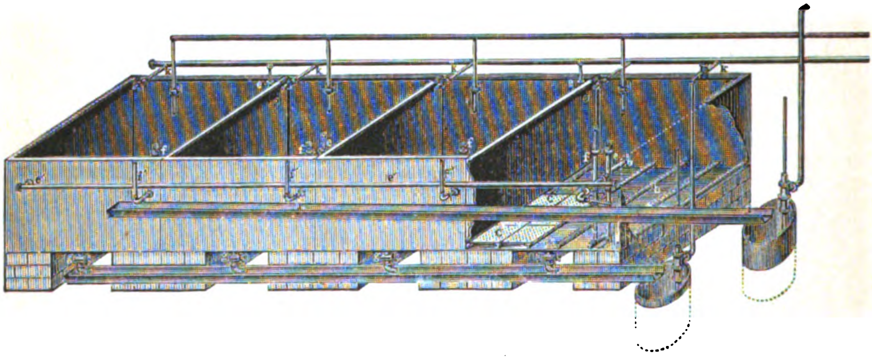

Fig. 37.

The way of carrying out the process is shown in Fig. 37. A number of 'tanks' or 'vats'—at least three, more commonly four, but sometimes five, six, or even more—is combined to form a set. The tanks must be all on the same level, and this should be so far removed from the ground, by means of pillars, that no leaks can occur without being observed. They are made of wrought iron. Near the bottom there is a row of T-pieces *bb*, for supporting the perforated plates *cc*, forming a false bottom. Whilst the true bottom is often made to slope to one side, where the outlet cock is placed, the false bottom must be quite horizontal. Each of the tanks contains two overflow pipes, one, marked *e*, for weak liquor, and another, marked *f*, for strong liquor. This is best seen on the section, Fig. 38. They are cast-iron pipes, a little wider in the upper part, with a conical plug fitting into a seat bored out at the enlargement. Above the plug-seat the pipe has a side-branch, bolted to one side of the tank, where there is a corresponding hole. The pipes pass through the false bottom, and the liquor can enter into them from below. If the plug is taken out, the liquor contained in the corresponding tank will rise from its bottom in the pipe *e* and will overflow into the next tank near its top, and thus a continuous stream of liquor may be produced right through the whole set of tanks. Where, however, it is intended not to run the liquor upon the next tank, because it is concentrated enough to be run off, the pipe *e* will be kept closed and the plug taken out of pipe *f*. All the pipes *ff* are arranged on the front side of the set; they are, on the outside, provided with swivel-pipes *f'*, which, when turned up, prevent the liquor from running out. By turning the branches *f'* downwards at the same time as the plugs are taken out, the strong liquor runs into the shoot *i*, and from this into the well, from which it is pumped into the settlers.

At some works there are cocks instead of the swivel-pipes *f'*; at others the strong liquor pipes *ff* are omitted, and the strong liquor is run off by means of the bottom-cocks *gg*, which must be provided in any case; but neither of these plans can be recommended. The bottom cocks *gg* serve for running away the weak liquor previously to casting out the solid waste. This liquor passes on to a separate well, from which it may be pumped into the water-conduit *k*, from which the tanks are supplied by a separate branch each. A special set of pipes serves for supplying either steam or hot water, as the case may be.

The working of the lixiviation vats is carried on as follows:—

Let us consider we have a set of four vats working in series, and that the spent black-ash waste has just been thrown out ('cast') from one of them. The empty vat is filled to about 1 ft. from the top with lumps of black ash obtained by roughly breaking the black ash balls with a sledge hammer into pieces a man can readily handle. The other three vats of the set during this time are working. The last of the series in which the black ash is nearly exhausted is fed with fresh water and maintained at a temperature not exceeding 35°C. The weak liquor so obtained is run to the weak liquor store tank. When the liquor leaving the weak vat has in this way been washed down until it shows no strength to the Twaddell hydrometer, the vat is allowed to drain by opening the bottom run-off tap *g*, after which the spent waste is thrown out and the vat is ready for filling again, or 'setting' with fresh black ash. The other two vats meantime have been working as follows: Weak liquor from the weak liquor store tank is run on to the partially exhausted or intermediate vat, and from it overflows by the pipe *e*, on to the strong vat. In this way a constant stream of partially-concentrated liquor, gradually dropping in strength from 36° to 0°Tw., is run through the strong vat where its strength is raised to 56°–36°Tw., or an average strength throughout the run of about 46°Tw. When the strength of the liquor leaving the strong vat has fallen to 36°Tw., it is no longer fit to remain a strong vat.

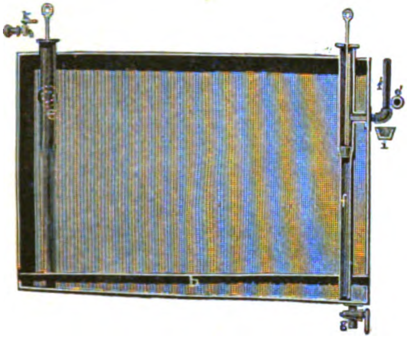

FIG. 38.

By this time also the intermediate vat is low enough in soda to become the weak vat and thus to take the place of the one just exhausted.

The freshly-charged vat mentioned above is then connected, the old strong vat becomes the intermediate vat, the old intermediate vat taking the place of the weak vat which has just been cast, and the whole series of operations starts again.

The great points to be observed are:—

1st. That the black ash should be as uniform as possible, so as all to lixiviate equally and rapidly.

2nd. That the lixiviation process should be conducted as quickly as possible with complete exhaustion.

3rd. That the temperature of the weak vats should not be allowed to exceed 35°C., and the strong vats 60°C.

4th. That the vat waste should be as completely exhausted as possible.

Testing methods for black ash, vat liquor, and tank waste. In order to test *black ash*, a sample consisting of several pieces of the ball (which unfortunately can never be a real average sample) is finely powdered, and 50 grms. of it are digested with tepid water, free from oxygen and carbonic acid; the solution is made up to 500 c.c., and is now tested just like the tank liquor obtained on the large scale. 1st, for *total available alkali*, by means of standard hydrochloric acid and methyl orange; 2nd, for *caustic*, by addition of barium chloride and titrating with hydrochloric or oxalic acid (in the last case without filtration); 3rd, for *sulphide*, by means of iodine; 4th, for *sulphate*, by means of barium chloride, either gravimetrically or volumetrically; 5th, for *total sulphur*, by oxidising with bleaching powder and estimating the sulphate formed; 6th, for *chloride*, by standard solution of silver nitrate, after having exactly neutralised the alkali by nitric acid and boiled away the H_2S; 7th, for *ferrocyanide*, by means of Hurter's copper sulphate solution. *Vat waste* is mostly only tested for *available soda* by treating a solution, obtained as previously described in the case of black ash, with CO_2, boiling, filtering, and titrating the clear portion; sometimes also for *total soda*, including the *insoluble* portion, which is a somewhat lengthy process. (Details of all these methods in Lunge's Technical Chemist's Handbook.)

The analyses by Jurisch, given in the first table on p. 46 (Chem. Ind. 1880, 441), show the composition of revolver vat liquors (abridging the three decimals to one).

A comparison between different systems of working is afforded by the figures in the second table on the next page, which give grms. of each constituent for each 100 grms. of available soda (as Na_2CO_3+NaOH) in tank liquor.

The vat liquor is always too muddy for immediate further treatment, and must be *settled* first. This will cause the vat waste mechanically carried away to subside; at the same time the action of the air will cause some of the ferro-sodium sulphide to be decomposed, and the FeS to be deposited along with alumina and silica, partly or entirely in the state of chemical combination.

THE MANUFACTURE OF CAUSTIC SODA FROM LEBLANC VAT LIQUOR.

Solutions of caustic soda have been made ever since soda was commercially used, especially by soap makers; later on by bleachers, paper makers, &c. Most of these prepared such solutions themselves; sometimes they bought them in the state of *caustic liquor*; but from the nature of things this could never be a large trade. Such a trade has only arisen since caustic soda has been manufactured in the *solid*

—	Average of four months		Highest figure		Lowest figure	
	Grms. per litre	On 100 parts available soda	Grms. per litre	On 100 parts available soda	Grms. per litre	On 100 parts available soda
Total Na_2O .	188·0	—	198·4	—	168·9	—
Na_2O as Na_2CO_3 .	147·9	—	161·2	—	131·7	—
Na_2O as NaOH .	40·0	21·3	47·7	24·8	37·2	18·7
Na_2CO_3 . .	252·9	—	275·6	—	225·2	—
NaOH . .	51·7	—	61·6	—	48·0	—
NaCl . . .	10·7	5·7	15·5	8·1	6·3	3·2
Na_2SO_4 . .	2·8	1·4	3·8	1·9	1·9	1·0
Na_2SO_3 . .	0·3	0·1	0·5	2·8	0·1	0·1
$Na_2S_2O_3$ . .	1·3	0·7	2·1	1·0	1·0	0·5
Na_2S. . .	4·1	2·2	5·0	2·7	2·9	1·6
Total Na_2SO_4 calcul.	13·1	7·0	14·7	8·0	10·7	5·7
Total Na_2SO_4 found	13·1	7·0	15·5	8·3	10·5	5·6
Na_4FeCy_6 . .	0·8	0·4	1·1	0·6	0·5	0·3
SiO_2, Al_2O_3, Fe_2O_3	4·7	2·4	5·6	3·0	3·8	2·1

—	Muspratt hand furnaces, 16 days' average	Muspratt revolvers, 30 days' average	Runcorn Soap and Alkali Works						More recent practice		
			Péchiney revolver			Péchiney-Weldon					
			average	highest	lowest	average	highest	lowest	average	highest	lowest
Na_2O as NaOH . .	33·6	21·3	13·3	15·2	8·5	19·1	21·5	15·2	25·0	30·0	21·0
NaCl	7·3	5·9	—	—	—	—	—	—	3·0	6·0	0·75
Na_2SO_4 . . .	6·0	1·7	4·1	5·4	2·8	3·6	4·5	3·2	2·3	4·4	1·25
Na_2SO_3 . . .	0·4	0·2	—	—	—	—	—	—	—	—	—
$Na_2S_2O_3$ . . .	1·1	0·7	1·5	1·6	1·2	1·0	1·3	0·9	—	—	—
Na_2S	1·4	2·1	1·4	1·8	0·9	2·2	3·0	1·9	1·0	1·5	0·5
Total Na_2SO_4 cal. .	10·9	6·8	9·5	10·6	7·8	9·4	10·8	8·0	—	—	—
Total Na_2SO_4 found .	10·9	6·8	9·3	10·4	9·0	9·4	10·8	0·6	4·9	6·5	4·2
Na_4FeCy_6 . . .	0·1	0·4	0·2	0·4	0·2	0·2	0·3	0·2	—	—	—
SiO_2, Al_2O_{31}, Fe_2O_3 .	2·7	2·4	—	—	—	—	—	—	—	—	—
Mixing proportions:											
Salt-cake 96 p.c. .	100	100	87·8	—	—	—	100	—	—	—	—
Limestone . .	102·1	76	64·4	—	—	—	74·4	—	—	—	—
Coal . . .	52·1	38	34·8	—	—	—	41·9	—	—	—	—
Mactear lime . .	—	8·3	—	—	—	—	—	—	—	—	—
Péchiney salt-cake .	—	—	12·2	—	—	—	11·6	—	—	—	—
,, limestone dust	—	—	7·3	—	—	—	7·0	—	—	—	—
Sifted cinders . .	—	10	—	—	—	—	—	—	—	—	—

state, which was first done about 1845 in Tennant's works at St. Rollox, but only experimentally. The development of that large industry only dates from 1853, and is intimately connected with the names of Gossage, Dale, Ralston, Gamble, Muspratt, Pauli, Deacon, and other Lancashire manufacturers. It was introduced much later into the Tyne district and abroad.

Solid caustic was originally only made from the caustic mother-liquor ('red liquor') obtained in concentrating vat liquors for Leblanc soda ash as hereinafter described. This source of caustic soda is now of little importance, owing to the practically complete replacement of Leblanc soda ash by ammonia alkali.

Some caustic is made by dissolving and causticising ammonia alkali; but the bulk of it is made from *vat liquors*, obtained in the usual way.

The Leblanc vat liquors, as shown in the analyses given above, contain 70–80 p.c. of the total soda as Na_2CO_3, and have first to be causticised or converted as completely as possible into NaOH. The proper performance of this operation plays a very important part in the manufacture of caustic soda.

The method adopted for causticising the Leblanc liquors is always by treatment with quicklime:

$$Na_2CO_3+CaO+H_2O=2NaOH+CaCO_3.$$

This is a reversible reaction, and the conditions under which it is performed govern the proportion of NaOH to Na_2CO_3 in the causticised liquor. The apparatus used is usually a large wrought-iron vessel, fitted with either horizontal or vertical mechanical agitators and a basket (*see b* in Figs. 39 and 40), into which the lime required is placed.

Formerly the agitation was frequently effected by steam or air, but these have been shown to be less economical than the mechanical agitator. The strength of liquor used for the causticising operation is important, there being two facts to be considered.

1st. The lower the strength of the liquor causticised the higher the proportion of the total soda which can be converted into NaOH by the lime.

2nd. The higher the strength of the liquor causticised the less fuel is afterwards required for concentration. As a compromise between these two factors it is usual to causticise at a strength which gives a causticised liquor of 20°–26°Tw. or 1·1–1·13 sp.gr. With careful work such a liquor will contain 91–92 p.c. of its total soda as NaOH.

The operation is usually carried out as follows: Well-settled vat liquor is heated as far as possible by waste heat or exhaust steam, and run into the causticiser where it is diluted to a strength 1·1–1·13 sp.gr. with weak liquor obtained from a later stage of the process, and by water, both of which should also be preheated when possible by waste heat. The quantity of total liquor in the causticiser should be sufficient to just cover the bottom of the cage *b*. The liquor is then heated to boiling by steam through the steam pipe, and the quicklime thrown in gradually. Care is required to prevent the causticiser from boiling over. The steam can now usually be shut off, the heat of hydration supplying heat to make good losses by radiation.

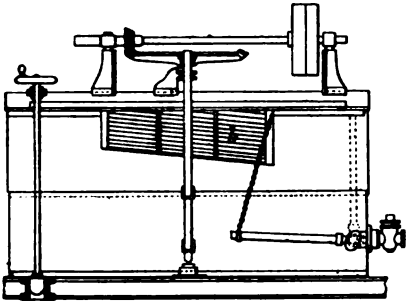

FIG. 39.

More vat liquor and weak liquor are gradually run in and the lime added until the causticiser is full and the calculated quantity of lime added. A sample should then be taken and tested to find the causticity per cent. obtained, and if this does not exceed 90 p.c. more lime is added.

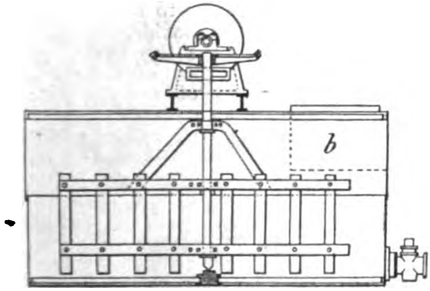

FIG. 40.

The agitator is then stopped and the liquor allowed to settle for about 1½ hours. The comparatively clear liquor is stripped off the top by a drop syphon and run to settlers. The causticiser then remains, perhaps, one-third full of caustic liquor and lime mud. This can either be run out direct on to a filter bed or the causticisers can be filled up with water, agitated and again settled. The weak liquor so obtained, together with washings from the filter, is used for diluting another batch of vat liquor. The washed mud is then run on to a filter bed and again washed with water.

It is by no means uncommon to work two or even three batches in a causticiser without running off the lime mud. This saves time and makes it possible to work each batch with a larger proportion of excess free lime than would be economical for the single batch. The increased quantity of free CaO slightly increases the causticity per cent. obtainable.

Many investigations have been made into the lime causticising operation, and several processes have been suggested with the object of increasing the proportion of causticised to uncausticised soda, *i.e.* of NaOH to Na_2CO_3 in the final liquor when working at higher strengths of solution.

Patents were taken out by Parnell (4144, 1877, and 2203, 1878), by Wells (3803, 1879), by Menzies (3804, 1879), and by Herberts (3577, 1882) for conducting the causticising operation under pressure, which was claimed to give increased causticity per cent. at strengths up to 1·2 sp.gr. The Parnell process was tried extensively on a large scale and failed.

The investigations of Lunge and Schmidt (Ber. 1885, 3286) showed that working under increased pressure did not increase the causticity per cent. obtained.

Herberts also, in a later patent (D. R. P. 43492), claimed that higher causticity could be obtained with liquors of 1·14–1·16 sp.gr. when working under diminished pressure. Later investigations on this subject are those of Bodländer (Zeitsch. angew. Chem. 1904, 1519), Leblanc and Novotny (Zeitsch. anorg. Chem. 11, 181), Wegscheider and Walter (Chem. Zentr. 1907; and Monatsh. 28).

At the present time, as mentioned above, however, the ordinary practice is to causticise at 1·1–1·13 sp.gr. and obtain about 91 p.c. of the total soda as NaOH.

The filters on to which the lime mud from the causticisers is run vary considerably in design and arrangement; Fig. 41, however, is representative of a large number of filters, and shows a thoroughly efficient and satisfactory apparatus.

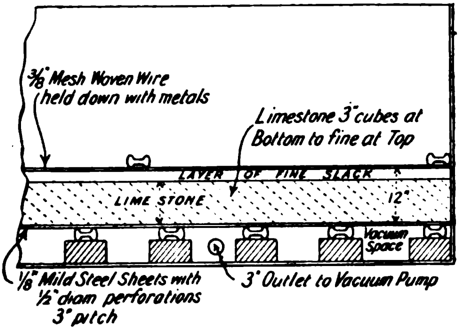

FIG. 41.

The lime mud is run from the causticiser through the 3- or 4-inch diameter pipe on to the filter bed and the vacuum pump started. As soon as the surface of the mud begins to dry cracks are likely to appear. These require raking over with a rake or patting with a spade to close them up. Hot water is then run on to the bed of mud to wash out the caustic liquor which is held up by and surrounds the particles of $CaCO_3$. Finally, the vacuum pump is kept going for some time to dry the mud as much as possible. Under the best circumstances, however, it will retain over 40 p.c., and usually nearly 50 p.c. of water.

On the care with which this washing process is conducted depends the quantity of soda left in the mud.

With careless washing, with cracks in the bed of lime or round the sides of the filter or holes and inequalities in the filter bed, there may be a heavy loss of soda.

With good work the soda loss can be reduced to well below 1 p.c. soda on the weight of lime mud; with bad work it may rise to 4 p.c., and even 6 p.c. on the mud.

As there are about 2 tons of lime mud to the ton of Leblanc 70 p.c. caustic soda, it is evident that this may be a very serious matter.

As mentioned above, the washings from the filters are used to dilute the vat liquor to the strength required for the causticisers.

Other forms of filter for caustic lime mud have been suggested of a more or less mechanical nature, but have not met with extended use, *see* patents by J. Brock and T. Martin, 2127, 1887; G. H. Bolton and T. A. Bullough, 14563, 1888; Hurter and Driffield; Solvay (Eng. Pat. 4725, 1896); and Houghton and the United Alkali Co. (Eng. Pats. 7957 and 28791, 1903).

The following analyses of caustic lime mud are given by Davis (Chem. News, 32, 187):—

$CaCO_3$	40·2	42·0
$Ca(OH)_2$	3·7	3·1
SiO_2	0·7	0·8
Al_2O_3	0·2	0·3
Fe_2O_3	—	0·7
MgO	0·1	0·1
Na_2O	1·8	1·6
H_2O	48·0	46·6
	99·6	99·6

Lime mud is frequently employed to replace part of the limestone required for the revolver charge. For this purpose it is used in the wet condition. The following shows a revolver mixing with and without lime mud:—

	1	2
Salt-cake	52·0	55 cwts.
Limestone	37·0	56 cwts.
Lime mud	45·0	
Mixing slack	21·0	22 cwts.

When used in this way the soda contained in the mud is probably recovered, and some limestone is saved. The output of the revolver is, however, reduced, and the labour and fuel charges increased per ton salt-cake decomposed. The advisability of utilising the lime mud in this way depends, therefore, on a balance in which the relative prices of limestone and fuel are the largest factors. In some works the attempt has been made to burn the calcium carbonate in the mud back again to quicklime, and it is reported that this has been economically done in the rotary kilns used in the manufacture of Portland cement. The lime mud is also used as a raw material for the manufacture of Portland cement (Rigby, J. Soc. Chem. Ind. 1888, 301).

A very important and increasing outlet for caustic lime mud is for liming the soil. For this purpose calcium carbonate is as useful as the oxide and the finely-divided condition of caustic lime mud renders it particularly suitable.

The lime improves the soil by opening up the land, this is especially valuable in the case of the heavier soils. It is in itself a plant food, and also helps to bring into action the insoluble reserves of nitrogen and potassium in the soil. It corrects acidity in the soil, and is the best remedy for the finger and toe disease in turnips and swedes. *See* leaflet No. 170 of the Board of Agriculture and Fisheries.

A totally different method of causticising is that of Löwig (Eng. Pat. 4364, 1882), who evaporated soda liquors with pure ferric oxide, and exposes the mixture to a bright-red heat. The mass is thus converted into sodium ferrate (or rather 'ferrite'), which is insoluble in cold water, so that it can be purified by washing with it: it is then treated with water at 80°C., which decomposes the compound into caustic soda and regenerates the ferric oxide. Thus concentrated liquors are obtained quite free from iron. In patent D. R. P. 41990 Löwig extends this plan to the sesquicarbonate or roaster ash of the ammonia soda process produced by the partial furnacing of the sodium bicarbonate first obtained to expel the NH_3, and part of the CO_2. This substance is then further treated with ferric oxide in a revolving furnace until the whole has been converted into a compound of soda, which is split up by the action of water into caustic soda and insoluble ferric oxide. The British patent of Mond and Hewitt (No. 1974, 1887) states that for the efficient conduct of the process it is necessary to use a pure sodium carbonate and oxide of iron, and to remove the liberated carbonic acid as it is formed. They also advocate the use of a revolving furnace similar to the black-ash revolver for the formation of the 'ferrite,' and the use of water gas as the source of heat in order to keep down the partial pressure of carbon dioxide.

The Löwig process has the advantage of yielding a stronger solution of caustic soda than the lime method of causticising. As mentioned above, the lime process produces a causticised liquor of 1·1–1·13 sp.gr., while the Löwig process produces one of 1·32–1·36 sp.gr., a difference which corresponds to a reduction in the quantity of water to be evaporated for the manufacture of solid caustic soda of about 6 tons water to the 1 ton 70 p.c. caustic soda.

For causticising liquors such as the Leblanc liquors above described, the process is out of the question, as before it can be worked those liquors have to be evaporated to dryness, and in addition there is the fuel required for the furnace and the other working costs which are heavier than in the lime process. The Löwig process is, however, used for causticising on a large scale the solid sodium carbonate obtained in the ammonia soda process, but it is doubtful even then if it is cheaper than the lime process.

Strontium hydroxide has been suggested as a substitute for lime in the causticising operation (Bacon, D. R. P. 99344), because the reaction is much more complete than in the case of lime, and can be carried out in stronger solution.

The process, however, has not been adopted, as far as is known, on the large scale.

The liquor from the causticisers at 1·1–1·13 sp.gr. contains 9–10 tons of water per ton of 70 p.c. caustic soda, and the economical evaporation of this large quantity of water has always been one of the technical problems of caustic soda manufacture. The usual custom is to do the first part of this evaporation by means of the waste heat of the black-ash revolvers as mentioned above. Fig. 36 shows a revolver with a series of the shallow wrought-iron bottom-heated pans *a, a, a, a, a* commonly used behind it.

The hot gases from the revolver dust stack pass under the series of pans, and the causticised liquor from the settlers is fed in a steady stream into the pan furthest from the revolver from which it overflows from pan to pan, until it leaves the front pan at, under good condition, 1·2 sp.gr. This means that the revolver waste heat has in this way evaporated 3–4 tons of water per ton 70 p.c. caustic soda out of the total 9–10 tons.

The further treatment of the caustic liquors to obtain solid caustic soda is divided into two stages, 'concentration' and 'finishing.'

The 'concentration' stage carries the liquor up to such a strength that the bulk of the Na_2CO_3 left in the causticised liquor (8–10 p.c. of the total Na_2O) and the Na_2SO_4 from the vat liquor (*see Analysis*) separate out, forming what are called 'caustic salts.'

The 'finishing' stage takes the liquor at 1·4–1·5 sp.gr., settled clear of 'salts,' evaporates the balance of the water, amounting to 1–2 tons per ton 70 p.c., and heats the fluxed anhydrous caustic soda to full redness.

The 'concentration' is usually now performed in large cast-iron self-fired vessels called caustic pots (*see* Fig. 42). These vessels are made of metal specially selected for the purpose, and vary in size in different works. A common size is 10 ft. diameter by 6 ft. deep.

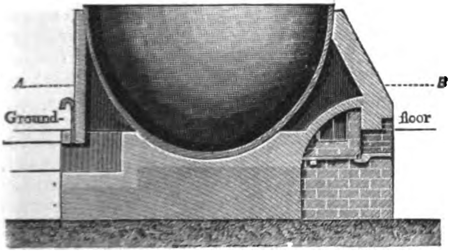

FIG. 42.

The setting of the caustic pot is a matter of importance, as the life of the pot, especially when used as a 'finishing pot' is largely dependent on the prevention of direct impact between a flame blast from the grate and the metal of the pot. It is usual, therefore, to protect the pot opposite the fireplace with a guard wall.

The pot is filled with liquor and fired. The loss by evaporation is made up by a constant slow stream of fresh liquor until the sp.gr. has risen to 1·4–1·5 as the case may be. The strength to which the liquor is taken in this stage depends on the strength of the caustic it is intended to pack. The fire is then drawn and the pot allowed to settle for some hours.

After settling the clear liquor is baled out with a large wrought-iron ladle cleverly balanced on the pot edge and worked with little exertion by an experienced man.

The clear liquor is either baled into an adjacent pot for the finishing operation or into a tank from which it is pumped to settlers where a further batch of salts settles out on standing and cooling.

The salts are fished out of the pot with a perforated ladle when all the clear liquor has been taken, and are drained as well as possible or jigged in a centrifugal machine.

The salts are a great source of trouble and expense.

The following analysis represents an average composition of the salts fished from the concentrating pots and jigged :—

	p.c.
Na_2CO_3	39
Na_2SO_4	20
NaOH	9

A small part of these salts is continually returned to the revolver to prevent too heavy an accumulation of Na_2SO_4 in the liquors, but the chief part is dissolved and mixed with the liquors feeding the causticiser and recausticised.

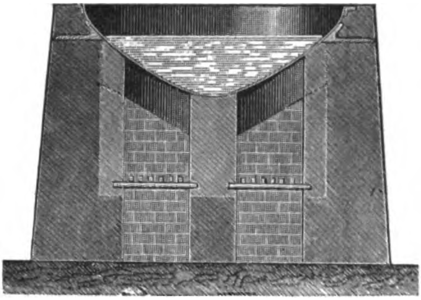

FIG. 43.

The total quantity of salts obtained per ton 70 p.c. caustic varies with the efficiency of the causticising operation between 5 and 7 cwts. Other methods of concentration have been suggested. One vessel frequently used, especially in former days, is the so-called boat pan, of which Fig. 43 is a cross section.

The boat pan is made of cast iron $1\frac{1}{8}$–$1\frac{3}{4}$ ins. thick, and its dimensions are about 12 ft. long, 8 ft. wide, 3 ft. 6 ins. deep.

Another method used for many years in some factories has been to concentrate the liquors up to a strength well short of the salting-point in Lancashire boilers, using the steam raised at low pressure for heating purposes. The difficulty is, however, that after a few years the boiler repairs become very heavy, and there is a great tendency for the rivet heads to shear off.

Recently multiple effect evaporation has been largely applied to caustic soda liquors with success.

Multiple effect evaporation consists in making use of the latent heat of the vapour evaporated from one liquid to generate vapour from a liquid with a lower boiling-point.

These liquors can either be really different liquids with different boiling-points, or, as in the case we are considering, the liquors can be the same, but by reduction of pressure the boiling-point of the second lot of liquor may be lowered sufficiently below the vapour temperature of the first lot to allow reasonable heat transference to take place.

The vapour raised from the second lot of liquor can be similarly used for evaporation of a third lot of liquor, whose boiling-point has been made still lower by a further reduction in pressure. The process can theoretically be repeated indefinitely, but actual multiple effect evaporators vary from two to six effects, *i.e.* the latent heat in the vapour originally evaporated is made use of from one to five times.

Fig. 44 shows a common form of an evaporator for use with caustic soda liquor in triple effect.

A. is the first effect.
B. is the second effect.
C. is the third effect.

The shells of these vessels are cast iron divided into three divisions by the tube plates *d*, *d'*.

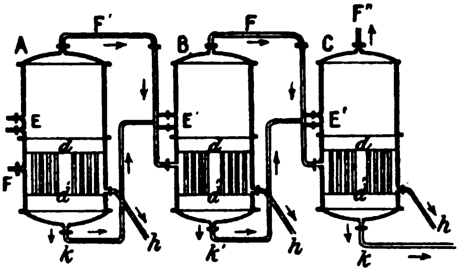

FIG. 44.

The tube plates themselves are connected by a number of wrought-iron tubes about 2 ins. diameter, and one central big tube all expanded into the tube plates top and bottom.

The space between the tube plates *d*, *d'*, through which the tubes pass, is the steam space and into it steam usually under pressure from boilers is admitted through F. In some cases the steam used in the first effect of an evaporator is exhaust steam.

In normal work the evaporator is filled with liquor through the inlet E to a few inches above the upper tube plate. The steam, therefore, is on the outside of the tubes, the liquor to be heated is inside them.

The weak caustic liquor is pumped into A by a pump not shown, and finally the concentrated liquor is drawn from C by a pump also not shown.

The steam raised from the liquor in A passes on through F' into the steam space of B, where it again raises steam from the liquor in B's liquor space. The steam raised in B passes similarly into C steam space, while the steam raised in C's liquor space passes away through F" to the condenser and vacuum pump not shown.

The speed at which work is done, *i.e.* the rate at which heat is transferred from the steam through the metal of the tubes to the liquor, depends first on the difference in temperature of the steam and liquors, and secondly on the circulation of the liquor in the liquor space. The liquor rises through ebullition in the small tubes from the bottom division of the evaporator to the top division, and then returns downwards through the big central tube. On the rapidity and uniformity in the different tubes of this circulation depends largely the heat transference per square foot of metal surface.

Another important type of evaporator is the Kestner so-called 'climbing film evaporator.' The essential point about this evaporator is that it contains a much smaller number of tubes than the type previously described, and that the liquor passes once only up the tubes in each effect. In this way the circulation is obtained by the direct action of the liquor-feed pump, and does not depend on the relative heating effects of small tubes and a large tube. The tubes in the Kestner evaporator are much longer, they are, however, about the same diameter, 2 ins., and are of wrought iron. In the older type the tubes are from 4 to 7 ft. in length, in the Kestner evaporator they are 23 ft. long.

Fig. 45 shows construction of a Kestner evaporator which explains itself.

Fig. 46 shows the arrangement of a Kestner four-effect evaporator, where A, B, C, D are the four effects, and E is the condenser. The general construction will be readily understood by comparison of Figs. 45 and 46.

The vessels *b*, *c*, *d*, *e* are save-alls or catch-boxes to collect any caustic liquor which escapes the baffles at the top of the evaporators and to prevent its loss.

The following is an example of the absolute pressure in the steam spaces of the four effects of such an evaporator, showing the gradual fall from effect to effect, on which the multiple evaporation depends.

Steam space	of	1st	effect	abs. press.	52 lbs.
„	„	2nd	„	„	35 lbs.
„	„	3rd	„	„	18⅛ lbs.
„	„	4th	„	„	7⅛ lbs.

Liquor space of the 4th effect abs. press. 1¾ lbs.

In such evaporators as have been described it is customary to concentrate the caustic liquors up to, but not beyond, the point at which salts begin to deposit, that is to about 1·3 sp.gr. For higher concentration an evaporator of the older type or the Kestner type, in either case with cast-iron tubes, is frequently used, either in single or double effect, more commonly in single effect. One way of working an evaporator of the older type is to fill it with the liquor at 1·3 sp.gr. and concentrate, adding more fresh liquor continuously to make good the loss by evaporation. Eventually when the evaporator is full of liquor at 1·4–1·5 sp.gr., as may be required, the bottom valve is opened and the whole contents, liquor and salts, allowed to fall into a settler or on to a filter bed. The salts are separated and the liquor is pumped to the store tanks feeding the finishing pots. With the Kestner type of evaporator, which holds practically no stock of liquor, the usual method of work is to start with 1·3 sp.gr. caustic liquor in a stock tank, and to circulate it round and round, through the evaporator and back to the stock tank, until the whole is up to 1·4–1·5 sp.gr.

Another method of work with the older type is to concentrate continuously, and not in batches, and to remove the salts from time to time from the bottom of the evaporator by means of a small closed vessel underneath it, which can be connected either with the atmosphere or the evaporator. Automatic arrangements have also been invented for continuous removal of the salts from the evaporators, and it is understood are used to some extent.

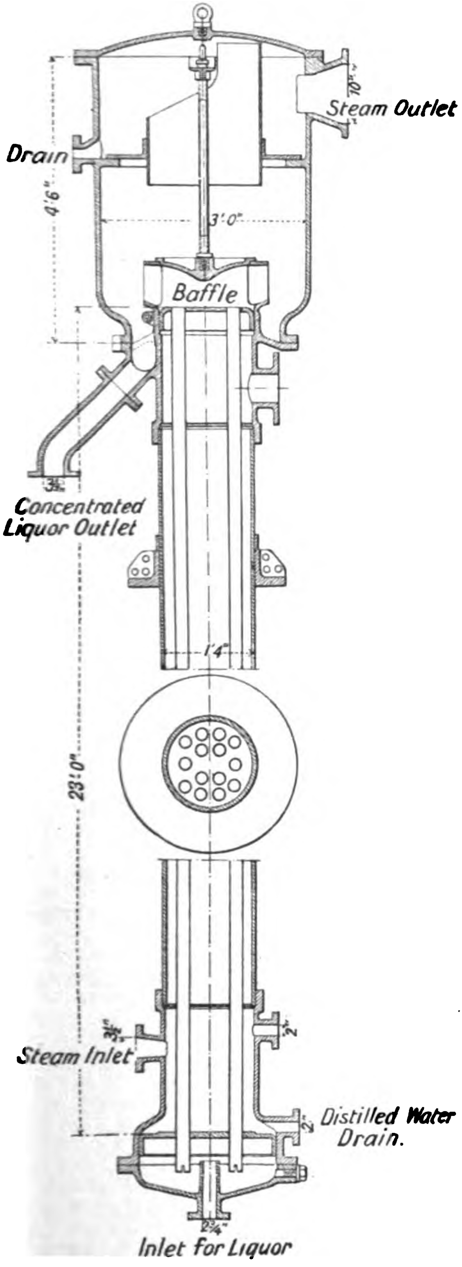

FIG. 45.

We have now the caustic soda solution as a settled liquor about 1·45–15· sp.gr. at 15°. This liquor is run into a caustic pot similar to that described above, for the concentration, and boiled.

A common way of working is to fill up two pots and concentrate until all the water is driven off, and then to bale the liquor from one into the other pot, and so make one full pot. The liquor, being of practically the same temperature in both pots, mixes without difficulty. At other times one pot is worked by itself and continuously fed with the 1·45 sp.gr. liquor. When the temperature of the pot increases and the flowing of this solution on to highly-heated, nearly anhydrous caustic becomes dangerous, it is usual either to sprinkle the liquor over the surface of the pot by running it through a perforated plate or ladle, or else to cover the pot with the loose wrought-iron lid which is, in any case, used as a cover during the last stage of the finishing. When all water is driven off, and the pot is full, the above-mentioned loose lid is put on and the pot gradually heated up until the molten NaOH in it is a just visible dull red colour.

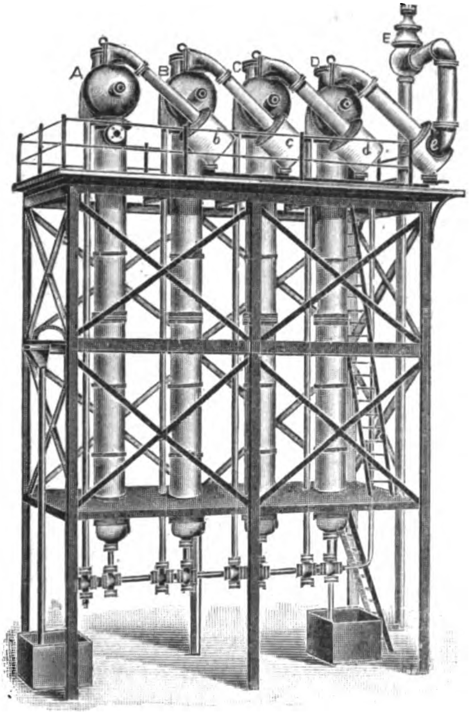

FIG. 46.

As caustic soda is usually sold at definite strengths, 60 p.c. Na_2O, 70 p.c. Na_2O, 76 p.c. Na_2O, &c., it is necessary to see how near the contents of the pot are to the required test.

A sample is, therefore, taken out on a spade or in a mould, allowed to set, and then tested in the laboratory. The caustic in the pot is usually found too high in test, and has to be reduced by the addition of a calculated and weighed quantity of well-dried salt (NaCl). The salt is added in small quantities through a lid in the sheet-iron cover mentioned above. The salt decrepitates badly when it comes in contact with the caustic soda, and causes considerable irritation to those near the pot by spreading finely-divided caustic through every outlet in the pot cover.

After addition of the salt the pot has to be again fired, as the fusion of the salt cools it considerably, and unless reheated it will not settle satisfactorily. The settling takes from 6 to 12 hours, and during this period the temperature gradually drops to about 330°. The quality of the caustic depends very largely on the settling of the impurities, which consist chiefly of ferric oxide, alumina, and silica. The clear settled caustic is then, after cooling to about 325°, ready for packing.

So far, one important point has not been dealt with, and that is the removal of the sulphide always present in Leblanc liquors. There has been much discussion as to the best way of doing this, and many expedients have been tried. Hargreaves proposed oxidation of the heated liquor by blowing air through it. In this case the oxidation was very slow and incomplete. Pauli advocated the addition of 'Weldon mud' (*see* art. CHLORINE, under heading *Weldon bleaching-powder process*) (Eng. Pats. 1306 and 1530, 1879). A detailed description of the oxidising process, both with air alone and by Pauli's process, has been given by Jurisch (Dingl. poly. J. 240, 55).

The removal of the sulphide by electrolysis was patented by Merle in 1875, and tried at Salindres; it was the subject of a later patent by Deacon, Hurter and Elmore (Eng. Pat. 800, 1885). Chance (Eng. Pat. 5920, 1885) decomposed the sulphides by a mixture of ferric and calcium hydroxides or carbonate, produced by precipitating ferric chloride with a large excess of lime or calcium carbonate.

The practically universal practice now is to remove the sulphide either by the addition of zinc oxide in the causticiser or by the addition of sodium nitrate to the finishing pots or both. The zinc oxide acts according to the equation:

$$ZnO+Na_2S+H_2O=ZnS+2NaOH.$$

Sodium nitrate probably acts in the finishing pot as follows:—

$$8NaNO_3+5Na_2S=5Na_2SO_4+4Na_2O+8N.$$

Metallic zinc readily dissolves in hot caustic soda liquor of about 1·13 sp.gr., and the solution so obtained is run into the causticiser during the causticising process.

The sodium nitrate is almost always now added in the finishing pot.

A common practice is to take out the greater part of the sulphide with zinc in the causticiser and then to finish the oxidation with sodium nitrate in the caustic pot.

It is important not to add the sodium nitrate until the pot temperature has become high, say between 420° and 470°. If the sodium nitrate is added before the pot is sufficiently heated, the caustic liquor has a great tendency to boil over.

The sodium nitrate is added until a small sample of caustic taken from the pot is only slightly blackened by a solution of lead acetate. When the whole of the sulphide is removed sodium manganate is formed in the caustic soda and colours the finished product green. If accidentally the limit is passed and on packing a blue or green colour is observed, it can be rectified by the addition of a small quantity of finely-divided sulphur.

By far the greater proportion of the caustic soda is packed solid in what are called caustic drums. The packing consists in ladling the molten caustic into the drums. It is usual to surround one side of the pot to be packed with a semicircle of drums into which the caustic is successively conveyed by a wrought-iron shute, which is moved from drum to drum.

The drums are cylindrical sheet-iron packages (*see* Fig. 47) with lap joints. The sheets are neither riveted nor welded, but rolled under pressure. In order to avoid leakage before packing it is necessary to cool the caustic down to a temperature near to the point of solidification.

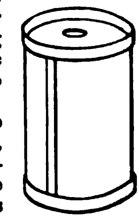
FIG. 47.

The clear liquid caustic in the upper part of the pot is packed, and then the residue called 'caustic bottoms,' which is a mixture of caustic soda, with the impurities settled out as above described, is baled similarly into drums.

The bottoms are of a deep-red colour, due to the ferric oxide they contain. The following is an analysis of a sample taken from a pot of 70 p.c. caustic:—

	p.c.
$NaOH$	63·2
Na_2CO_3	1·6
Na_2SO_4	2·0
$NaCl$	5·4
Na_2S	0·1
Na_2SiO_3	2·4
$Na_6Al_2O_6$	14·2
Fe_2O_3	10·9
	99·8

The 'bottoms' vary in strength between 53 and 63 p.c. Na_2O depending on the strength of the caustic from which they are made.

For many purposes the solution of 'caustic bottoms' after well settling is as efficient per unit of free Na_2O as that made from white caustic itself. The 'bottoms' are either sold at a reduced price as 'caustic bottoms,' or are dissolved, and the well-settled solution returned to the process.

As a package caustic drums are cheap, and from the fact that the caustic is a solid block, caustic in drums stows well for transit. On the other hand, caustic drums containing a solid lump of caustic weighing 6 cwts. are not readily handled by inexperienced hands. The best way to open a drum of caustic and break up the lumps is as follows: Lay the drum on its side with the seam upwards, and then crack the caustic by striking the drum along the seam once or twice for its full length with a sledge hammer. Insert a chisel under the seam and lever it open. The two ends should then fall off, and the caustic can easily be separated into pieces by simply inserting the chisel into the cracks and prizing them apart.

Caustic soda solution as such is sold to some extent usually in one of three strengths:—

90°Tw. containing	32·2 p.c. Na_2O
100°Tw. ,,	36·2 ,,
105°Tw. ,,	38·2 ,,

The solution is carried either in welded iron drums or in iron tank waggons.

Caustic soda is also sold in a form called 'detached,' that is thin sheets broken into small pieces and packed in casks.

The 'detached' caustic is usually made by baling a thin layer of the molten caustic on to heavy iron plates, where it almost immediately solidifies, and can be broken and packed. An apparatus to do this work was invented by Boulouvard (D. R. P. 34040).

Menzies (Eng. Pat. 4274, 1879) and Harned (Eng. Pat. 4677, 1883) described apparatus for grinding to a powder and sieving caustic soda. Caustic soda powder is produced to some extent for the market.

The commercial methods of analysis of caustic soda are given in Lunge's Technical Chemists' Handbook, p. 184.

Cream caustic. This is an inferior quality, formerly made, but now practically unknown. It was made by concentrating caustic liquor as described above until only about 12 p.c. water was left, and the caustic tested about 60 p.c. Na_2O.

The following are some analyses of commercial caustic soda of different strengths:—

		Huson and Hardwick		
	78 p.c.	77–78 p.c.	76 p.c.	70 p.c.
$NaOH$ . . .	98·1	96·92	95·4	86·6
Na_2CO_3 . . .	0·9	1·45	2·0	2·7
$NaCl$ . . .	0·4	0·58	1·5	6·9
Na_2SO_4 . . .	0·2	0·73	1·1	3·2
Na_2SiO_3 . . .	0·6	0·32	0·2	0·5
Fe_2O_3, Al_2O, and CaO	trace	trace	0·1	trace
Insol. . . .	—	—	—	0·2
	100·2	100·00	100·3	100·1

Production.—Of the total Na_2O charged into the revolver as salt-cake the average production in the form of finished caustic soda is about 85 p.c.

The greater part of the 15 p.c. loss is carried away in the black ash waste, partly as soluble soda through imperfect washing of the black ash in the lixiviating vats, and partly as insoluble compounds with the alumina and silica derived from the ash of the mixing fuel, the revolver lining, and the limestone.

Leblanc soda ash. As already mentioned, the original Leblanc process was introduced, and for many years worked primarily for the manufacture of sodium carbonate or soda ash.

For this purpose the same type of revolver was used, and black ash made as for the caustic soda manufacture just described.

The charge for the revolver was practically identical with the all-limestone charge given under caustic soda manufacture, viz.:

Salt-cake	55 cwts.
Limestone	56 ,,
Mixing slack . . .	22 ,,

The process of manufacture was the same as for caustic soda, up to and including the working of the lixiviating vats.

From the vats the liquor was pumped into settlers, where it was kept sufficiently warm to avoid crystallisation of the $Na_2CO_3,10H_2O$. A large amount of work was done on the purification of the vat liquor from iron in solution (chiefly as a double sulphide), from silica and alumina, and from ferrocyanides, but the usual practice was to take the well-settled vat liquor directly for concentration for ash. References to the papers and patents on the purification of vat liquor are as follows:—

Hurter (Chem. News, 39, 25), Carey, Gaskell and Hurter (Eng. Pats. 1161, 1881; 2939, 1879; and 5310. 1882), Newall and Sisson (J. Soc. Chem. Ind. 1887, 349), Mathieson and Hawliczek (D. R. P. 40987, 1887), Pauli (Eng. Pats. 1306 and 1530, 1879).

Figs. 34 and 35 (p. 41) show a black-ash revolver fitted with the top-heated pans adopted generally for the concentration of vat liquor for production of ash. In Fig. 34 *n*, *n'* are shallow open pans.

When properly settled, the vat liquor was run into the revolver pans *n*, *n'* (Fig. 34) until they were nearly full. The fire gases from the revolver passing over the pans concentrated the liquor, which was continually replaced by fresh liquor from the store tanks. Eventually the pans became full of a magma of crystals of Na_2CO_3,H_2O, which naturally formed first at the end nearest the revolver. It was the duty of the man in charge to work these salts to the back of the pans. When the operation was over the screw bolts were undone, the doors *p*, *p'* (Fig. 34) opened, and the salts raked out into the drainers *o*, *o'*.

The waste heat from the revolver passing over such a pan as is shown in Figs. 34 and 35, concentrated all the vat liquor made by the revolver separating the soda into crystals of fairly pure Na_2CO_3,H_2O in the drainer, and a liquor called red liquor, containing chiefly caustic soda, but also a little carbonate, and the main part of the impurities of the vat liquor. With a good vat liquor the mother or red liquor contained 20–30 p.c. of the total soda.

The composition of well-drained Leblanc pan salts was approximately as follows:—

Na_2CO_3	78·1
$NaOH$	0·3
$NaCl$	0·2
Na_2SO_4	0·4
Na_2SO_3	0·2
$Na_2S_2O_3$	0·3
Insol.	0·9
Water (by diff.) . . .	19·6

The salts after well draining were heated to redness in a reverberatory furnace when the non-carbonated liquor left in the salts was carbonated (sometimes sawdust was added to the salts to aid the carbonation), the water was driven off, and the small quantity of organic material present destroyed.

The soda ash then produced had a test varying in accordance with the draining of the salts from 50 to 57 p.c. Na_2O.

The following is an analysis of Leblanc soda ash made from well-drained salts:—

	p.c.
Na_2CO_3	96·5
$NaOH$	0·1
Na_2SO_4	1·1
$NaCl$	0·5
SiO_2	1·1
$Fe_2O_3+Al_2O_3$	0·5
MgO	0·2
	100·0

The operation of finishing soda ash is mechanical, but required continuous attention and work from the furnace man. In 1876 Mactear invented his mechanical finishing furnace, which was largely adopted. It consisted of a horizontal circular revolving hearth 20 ft. in diameter, made of boiler plate lined with firebrick. The following sketch indicates the general construction.

A purer form of sodium carbonate used to be made by dissolving the ash produced as above described in water—frequently with the addition of a little bleaching powder. The solution was well settled, and boiled down until it became a magma of crystals of monohydrate. The crystals were drained and furnaced, as in the case of the pan salts described above. The product so obtained was placed on the market as refined alkali.

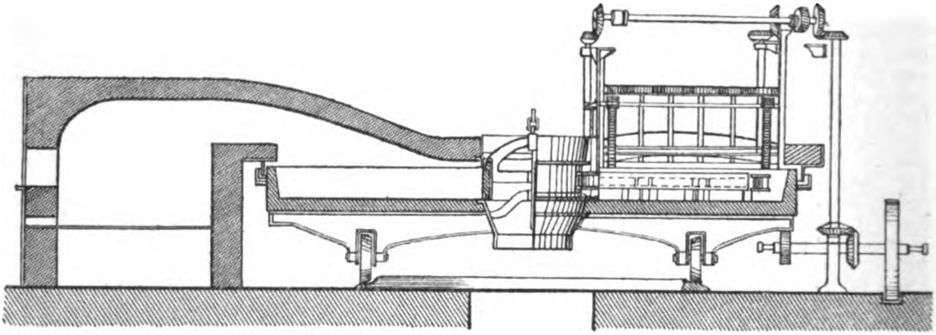

Fig. 48.

Soda crystals. *See* under *Ammonia soda.*

Crystal carbonate. *See* under *Ammonia soda.*

Bicarbonate of soda. *See* under *Ammonia soda.*

RECOVERY OF SULPHUR FROM THE VAT WASTE.

The alkali waste was for many years a great nuisance, not only to the manufacturers, but to the neighbourhood of the factories producing it. The waste, under the influence of moisture and the oxygen and carbonic acid of the atmosphere, decomposed on the waste tips on which it was deposited, giving off a strong smell of H_2S, and contaminating all drainage of surface water which passed through it. As is evident from the description of the Leblanc soda process, this waste contains the sulphur originally burnt in the pyrites, and formed into sulphuric acid, and which then passed by decomposition with common salt into the sodium sulphate charged into the black-ash revolvers.

The obvious remedy for the nuisance as well as to avoid the loss of sulphur was to recover the sulphur from the waste, and for many years work was done and processes were invented to this end.

As the difficulty was finally solved by the Chance-Claus process, it will suffice to do little more than mention the principal processes previously invented and tried.

J. L. Bell in 1852, Ward 1862, Hewitt 1877, Kynaston 1885, Parnell and Simpson, Schaffner 1862, Mond 1862, Schaffner and Helbig 1878, proposed processes for this purpose.

The processes of Mond and Schaffner were both worked for some time on the large scale, and both depended on the partial oxidation of the CaS in the waste by the oxygen of the atmosphere which rendered a considerable proportion of the sulphur soluble in the form of CaS_2H_2, CaS_2O_3, and polysulphides. The solution so obtained on addition of hydrochloric acid deposited sulphur.

The Schaffner and Helbig process depended on the power of $MgCl_2$ to decompose CaS at the boiling-point, and the process was expressed by the following equations:—

1. $CaS+MgCl_2+H_2O=CaCl_2+MgO+H_2S$.
2. $CaCl_2+MgO+CO_2=CaCO_3+MgCl_2$.

A good account of this process is given by Chance in J. Soc. Chem. Ind. 1882, 266.

Other processes were those of Kraushaar, Dingl. poly. J. 226, 412, and Alkali Inspectors' Report, 1877–1878, 15 and 35; Opl's process, D. R. P. 23142; Miller and Opl process, Eng. Pat. 2334, 1884. The last-mentioned process was tried at the Rhenania Chemical Works (*see* Hasenclever, Chem. Ind. 1889, 434).

The Chance-Claus process depends on a reaction originally observed by Gossage, who, in 1837, patented (Eng. Pat. 7416, 1837) a process in which the calcium sulphide of the alkali waste was decomposed by carbon dioxide.

Gossage himself failed to make the process technically successful.

Since his time others, viz. Opl, Rawes (Eng. Pat. 1393, 1882), Claus (Eng. Pat. 5958, 1883), proposed processes depending on this decomposition.

The reaction is

$$CaS+CO_2+H_2O=CaCO_3+H_2S.$$

The difficulty was to find an outlet for the sulphuretted hydrogen. The earlier efforts to utilise fuel gases or gases from inefficiently-worked lime-kilns with a low percentage of carbon dioxide gave a gas too weak in sulphuretted hydrogen to burn by itself.

Chance made use of lime-kiln gas from a more efficiently-worked lime kiln, and also showed the way to get a gas richer in sulphuretted hydrogen by taking advantage of the fact that the first reaction on carbonating a slurry of alkali waste is

$$CO_2+2CaS+H_2O=CaCO_3+CaS_2H_2.$$

This means that at first a portion of the carbon dioxide is absorbed, but no sulphuretted hydrogen is given off. By allowing the inert gases present with the CO_2 to pass away during this stage of the process a double equivalent of sulphuretted hydrogen is liberated in the final stage for each equivalent of carbon dioxide.

$CaS_2H_2+CO_2+H_2O=CaCO_3+2H_2S$.

The Chance process is described in Eng. Pat. 8666, 1887, and in a lecture by Mr. A. M. Chance (J. Soc. Chem. Ind. 1888, 162).

The process was worked by Chance at Oldbury, and the gases enriched as above described contained about 33 p.c., or even 38 p.c. of sulphuretted hydrogen.

At first it was attempted to utilise the sulphuretted hydrogen as a source of sulphuric acid. The dilution and varying strength of the gas obtained, and a material drop in the price of sulphur in pyrites prevented this plan from succeeding economically. It was not until C. F. Claus published his patent 3608 of 1882 that Chance was able to develop his process on successful lines. Claus showed that it was technically possible to burn sulphuretted hydrogen under such conditions that the oxygen combined with the hydrogen only, and the bulk of the sulphur could be obtained at once in a marketable form.

The reaction utilised by Claus is represented by the following equation: $H_2S+O=H_2O+S$.

Further Claus patents are Eng. Pats. 5070, 5958, 5959, and 5960, 1883).

The following is a description of the plant and method of work usually employed at present in carrying out the Chance-Claus process.

Alkali waste as fresh as possible is mixed with water into a cream of 1·2–1·25 sp.gr. in an iron vessel fitted with a mechanical agitator. From the mixer the waste is usually run into another similar vessel passing on the way through a coarse mesh sieve to remove cinders and lumps. The second vessel acts as a store, and is also fitted with a mechanical agitator to keep the waste from settling.

From this store tank the cream of waste is pumped by a large ram pump into a shute which feeds the series of carbonators in which the waste is treated with carbon dioxide.

The carbonators are strong cast-iron vessels, arranged usually seven in a series. Fig. 49 shows a carbonator.

The carbonators are cast in two parts, as shown above, and are usually about 7 ft. in diameter by 15 ft. high. The fresh lime-kiln gas is pumped first into the nearly spent carbonator, and then on through the series to the freshly-charged cylinder at the other end.

The somewhat elaborate pipe connections necessary to enable any one cylinder to act as a leading cylinder are shown in diagram in the patent specification of Chance and Chance (Eng. Pat. 8666, 1887) and described in Chance's paper above referred to.

From the carbonators the issuing gas passes into a gas holder of considerable size. Chance's own gas holder was 50 ft. diameter with a 14-ft. lift and held about 30,000 cu. ft. of gas. The gas holder plays an important part in neutralising the fluctuations in the strength of the sulphuretted gas produced.

The working of the carbonators when the Chance enrichment process is used was described by Chance as follows:—

'At 7 P.M. Nos. 7 and 1 vessels (Fig. 50, where the discs represent the 7 carbonators of a series) were charged with fresh waste. The lime-kiln gases were pumped direct into No. 3 vessel, and then through vessels 4, 5, 6, 7, and 1 by opening all the intermediate taps; the useless gases escaped from No. 1 vessel into the exit main, and thence through a purifier into the air for a period of 1 hour 40 min.

'At 8.40 P.M. the sulphuretted hydrogen gases from No. 5 vessel were sufficiently strong for use, the calcium sulphide having mostly been converted into calcium sulphydrate; the sulphuretted hydrogen gases taken from No. 5 tested over 30 p.c. H_2S, while the useless gases from No. 1 tested only 1 p.c., thus showing that vat waste is a very efficient absorber of sulphuretted hydrogen.

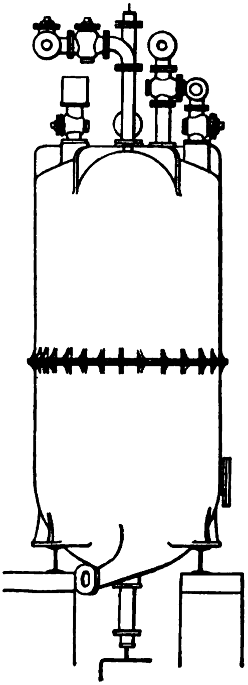

FIG. 49.

'The connections were then altered so that the H_2S gases could be taken from No. 5 to the gas holder. No. 2 vessel containing the partially carbonated waste was put into series, and the lime-kiln gases were now pumped through Nos. 2, 3, 4, 5, the sulphuretted hydrogen gases from No. 5 continuing to be taken to the gas holder for a period of 2 hours 25 mins., till 11.5 P.M. It was then found that the sulphuretted hydrogen gases were under 30 p.c., and that Nos. 2 and 3 were carbonated so thoroughly that water filtered from the mud did not tinge lead paper; Nos. 2 and 3 were, therefore, emptied and recharged.'

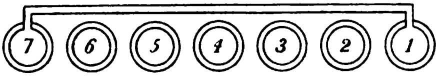

FIG. 50.

Much difficulty was experienced in working the enrichment process when the Chance plants were started, and it has been in most cases abandoned.

The following description shows, with the aid of the diagram Fig. 50, the method of working without enrichment.

No. 3 vessel is the leading carbonator into which the lime-kiln gases are first pumped, and is, therefore, the most nearly finished.

The gases pass from No. 3 through Nos. 4, 5, 6, 7, and 1 carbonators, No. 1 being the last charged, and from No. 1 to the gas holder.

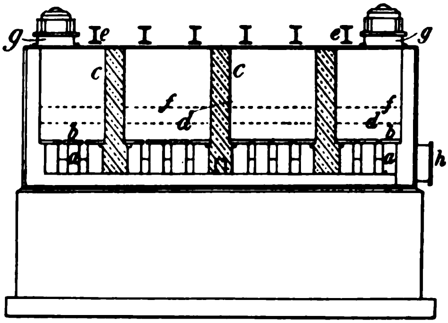

Fig. 51.

No. 2 carbonator is empty and ready for recharging.

The lime-kiln gases are pumped into No. 3 carbonator until the liquor in it no longer blackens lead paper. No. 3 is then finished, and is disconnected, No. 4 becoming the leading cylinder. No. 2, which has in the meantime been refilled, is connected up to the series, and becomes the final cylinder from which the gases pass to the gas holder under sufficient pressure (about 8 ins. water) to maintain the weight of the holder, and thus supply the pressure necessary to drive the gases on through the remainder of the plant.

It is usual to work the carbonators in 2, 3, or 4 sets of 7 vessels each in parallel, the number depending on the quantity of waste to be treated. By this means also the effects of the inevitable fluctuations in strength of the gas are materially reduced. Two such sets will deal with the waste from 300 tons salt-cake a week. It is obvious that the strength of the sulphuretted hydrogen produced, as well as the power consumed in pumping the lime-kiln gas through the carbonators, depends on the steady composition and percentage of carbon dioxide in the lime-kiln gases themselves.

Chance, in his lecture already referred to, gives great credit to Mond for his improvements in the working of lime kilns, and acknowledges the assistance received from him in this part of the process. Chance goes on to say, 'from the best-worked lime kiln, however, the escaping gases never contain on an average more than 30 p.c. CO_2.'

Further experience in working has somewhat increased the amount of carbon dioxide in lime-kiln gas.

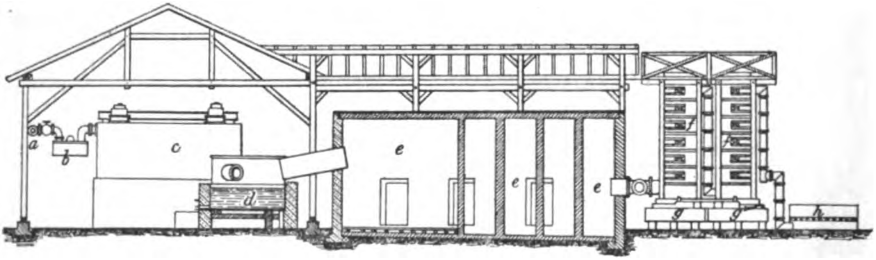

Fig. 52.

Two points about the lime-kiln gas in addition to its content of carbon dioxide are of great importance for this process.

1st. It is essential the gas should be practically free from oxygen, as oxygen in the gases pumped through the carbonators oxidises part of the sulphur in the waste to sulphite and thiosulphate, and prevents its recovery.

2nd. It is also important that the kiln gases should be practically free from carbon monoxide because the combustion of this gas together with the sulphuretted hydrogen in the Claus kiln liberates additional heat, which, as will be seen later, reduces the efficiency of the Claus kiln.

We have now in the gas holder when working with a lime-kiln gas containing 30 p.c. CO_2, a gas which :—

1st. When enriched by Chance's nitrogen elimination process contains 30–33 p.c. H_2S.

2nd. When not so enriched contains about 25 p.c. H_2S. These figures, of course, depend on the valves that regulate the distribution of the gases to the carbonators being in good condition and not leaking.

The gas from the gas holder then passes through a small vessel called a mixer, into which a carefully regulated supply of air is pumped by a blower or fan, and then through a water lute into the Claus kiln.

Fig. 51 shows a section of an average-sized Claus kiln.

The kiln is made of wrought-iron plates, and is 25 ft. in diameter by 9 ft. deep. It is brick-lined, and has a table of perforated tiles on which the packing is placed.

1st. About 12 ins. of broken fire brick.

2nd. 12 to 24 ins. of bog iron ore. Water lutes act as safety valves in case explosion takes place.

The mixed gases, *i.e.* the gas from the holder and the air, pass through the water lute *b*, into the top of the kiln above the packing. The gases pass downwards and out through the exit pipe *h* into a cast-iron receiver *d*, Fig. 52, which collects the bulk of the sulphur in a liquid form. The gases pass on from *d* into the brick chamber *e*, which contains several baffle walls, and in which almost all the remainder of the recoverable sulphur is collected as a coarse powder. The towers *f f* are very openly packed wooden scrubbers, which serve to collect an additional quantity of powdered sulphur. The Claus-kiln reaction is not complete, and always an appreciable proportion of the total sulphur passes away as sulphuretted hydrogen and sulphur dioxide with the exit gases.

From the exit *f f* it is usual to pass the gases through a furnace to burn the undecomposed sulphuretted hydrogen to sulphur dioxide before passing them on to the chimney.

Lunge states (Sulphuric Acid and Alkali, vol. iii. 11, 975) that of every 100 parts of sulphur entering the Claus kiln, 85 parts are recovered as refined sulphur and 15 p.c. is lost as sulphur dioxide and sulphuretted hydrogen, and polythionic acids.

This figure agrees very closely with the loss to be expected when the exit contains about 16 grns. S per cubic foot of gas, and the initial strength of the holder gas is 25 p.c. H_2S.

The bog-iron ore does not require renewal for many years, and has, in some cases, remained unchanged for over 20 years.

The working of the process is controlled by frequent tests of the exit gases from the Claus kiln for SO_2 and H_2S.

The method adopted is to obtain the total sulphur present, as SO_2 and H_2S, by drawing the gases through a known volume of standard iodine solution containing a little starch solution until the blue colour disappears, and noting the volume of gas aspirated.

The actual sulphur dioxide in the gases is determined by drawing a known volume of the exit gases through water containing hydrogen peroxide and then titrating the sulphuric acid formed with standard soda solution, using methyl orange as indicator. The difference between the total sulphur per cubic foot and the sulphur present as sulphur dioxide is taken as the sulphur present as sulphuretted hydrogen. The result in this country is usually expressed as grains total sulphur per cubic foot, and as grains sulphur as H_2S, and grains sulphur as SO_2 per cubic foot.

The air supply is adjusted in accordance with the relative proportion of sulphur as H_2S and SO_2. If the mixture of gases is thoeretically correct there should be obviously 2 H_2S to 1 SO_2, that is to say, if the total exit is 15 grns. sulphur per cubic foot the sulphur as H_2S should be 10 grns., and as SO_2 5 grns. per cubic foot.

In practice it is usual to work with as nearly equal quantities of sulphur as H_2S and SO_2 per cubic foot as possible in the exit gases.

The efficiency of the sulphur recovery depends entirely on the regularity of these tests, and the care with which the air supply is regulated. The completeness of the reaction is largely affected by temperature. An increase in the Claus-kiln temperature is always followed by an increase in the exit tests, and in the proportion, therefore, of sulphur not recovered.

A Claus kiln, as above described, will make 15–20 tons of sulphur per week, but with 30 tons per week the temperatures are too high, and the exit tests materially raised.

With 15 tons sulphur per week the temperature of the exit gases taken 1 ft. from the kiln outlet is about 290°C., which may be considered a good working temperature.

A number of attempts have been made to improve the Claus-kiln action by substituting other materials for bog-iron ore. Bauxite is recommended by the Chemische Fabrik Rhenania and Projahn (Eng. Pat. 3122, 1906), and is now largely used. The Rhenania in Chem. Zeit. 1908, 249, states as the result of several years' trial of this substance that there is a material reduction in the Claus-kiln exit tests.

Titaniferous iron ore (Eng. Pat. 25976, 1907) and manganese dioxide have both been tried, but so far as is known have not been successful.

Many efforts have been made to utilise the sulphur in the Claus-kiln exit gases, and it has been suggested :

1st. To burn the exit gases completely to sulphur dioxide and pass them along with pyrites gases into vitriol chambers (*see* Alkali Inspectors' 28th Report) and also through the Hargreaves' salt-cake plant (*see* Alkali Inspectors' 29th and 30th Reports). The 38th Alkali Inspectors' Report states that all attempts to deal with Claus-kiln exits in vitriol chambers have been unsuccessful.

2nd. To burn the sulphur completely to sulphur dioxide and utilise it for production of sulphur trioxide by the contact process (Carey and Heslop, Eng. Pat. 10317, 1900).

This process has not been adopted.

3rd. By absorption in milk of lime and by the slurry from the carbonators, *see* Alkali Inspectors' Reports for 1903 and 1904, and Heaton, Eng. Pat. 21217, 1890.

With the improved exits obtained by careful working, especially when the bauxite packing is used in the Claus kilns, no difficulty is experienced in turning the exit gases, after complete burning in a furnace, into the atmosphere through a chimney without raising the SO_3 test of the chimney gases above the statutory limit.

We have still to deal with the contents of the carbonators after removal of the sulphur. These are calcium carbonate and a weak solution of soda salts, chiefly sodium bicarbonate.

The following analyses of the calcium carbonate and the carbonator liquor are given by Chance.

Recovered calcium carbonate on dry	
Calcium carbonate	87·16
„ sulphate .	0·49
„ chloride .	—
„ silicate .	2·3
Magnesium carbonate	1·03
Sodium carbonate .	0·55
„ sulphate .	0·21
„ silicate .	1·42
Al_2O_3 . . .	1·47
FeS . . .	0·71
Coke . . .	2·06
Sand . . .	0·56

Water filtered from carbonator mud in grns. per gallon	
Soda (present as $NaHCO_3$) .	476·3
$CaCO_3$ . .	124·3
Total S . .	25·9
S as SO_4 . .	1·0
as hyposulphites	12·85
as sulphides .	Nil

The recovered calcium carbonate contains all the $CaCO_3$ used in the revolver mixing, and Chance originally suggested its use in the revolver over again. Mason (Eng. Pat. 21314, 1901) proposes to mould the Chance process waste into blocks before use in the revolver.

As far as is known, however, the carbonator mud is not used in the revolvers at present.

Another proposition has been to utilise the Chance waste for the manufacture of Portland cement.

Chance waste has been actually used for this purpose by Rigby (J. Soc. Chem. Ind. 1890, 254), and for many years by Chance himself.

The Chance waste is also an excellent form of calcium carbonate for agricultural purposes, and is largely used in the districts surrounding the Chance sulphur recovery plants (*see* remarks on this subject under *Caustic lime mud*, p. 48).

Chance also drew attention in his original paper to the value of the water filtered from the Chance waste for use on the black-ash vats, to which it would return quite an appreciable part of the total soda loss on the Leblanc process (*cf.* Eng. Pat. by Carey and United Alkali Co., Ltd., 7404, 1911).

With the discovery and practical success of the Chance sulphur recovery process the Leblanc process was materially cheapened, and a complete cycle of processes created.

The sulphur in pyrites passes through the following series of steps, finally emerging as a very pure form of commercial sulphur. The sulphur starts in the pyrites, passes into sulphuric acid, into sodium sulphate, into black ash as calcium sulphide, into sulphuretted hydrogen, and finally into pure sulphur. The production, of course, varies with the efficiency of the plant, but the sulphur recovered represents 65–80 p.c. of the sulphur in the salt-cake charged into the revolver.

2. The Manufacture of Soda by the Ammonia Soda Process.

The first germ of this process, which has quite revolutionised the alkali trade, is, as usual, found to have originated in various quarters. A German chemist, Vogel, is said to have known the reaction as early as 1822, and a Scotch chemist, John Thom, seems to have actually made some soda, in a crude way, by that process in 1836. Mond has definitively disposed of the attempt made by several French *savants* to claim the merit of the invention of this process for their countrymen, Schloesing and Rolland. Quite recently a claim has been set up for Fresnel, who is said to have made soda from common salt and ammonium carbonate in 1811, according to some hints found in recently-discovered private letters; evidently he did not meet with much success, as nothing came of his attempts. It is beyond doubt that the real history of the ammonia process dates from June 30, 1838, on which day Harrison Grey Dyar and John Hemming, both chemists residing in London, patented a process embodying all the principal reactions now carried out. This was done even more clearly in an additional patent, taken out in France on May 18, 1840, on their behalf, by Delaunay, where the use of a current of carbonic acid is first mentioned. A number of patents by other inventors followed, among which that of Gossage (1852) is remarkable, and those of Schloesing and Rolland (1854 and 1858) have become best known by the detailed description they gave in 1868 of their process.[1] Although their apparatus was very ingenious, it must have been deficient in important portions, for they could not make their works pay, and the reasons given for their abandoning the process are quite inconclusive.

In many other places works had been erected for making ammonia soda: by Dyar and Hemming, in Whitechapel; by Muspratt, at Newton; by Gossage and Deacon, at Widnes; and by a number of French and German manufacturers. But although we find every feature of the now-successful processes in these older establishments, there was always something or other wanting, and especially the loss of ammonia seems to have been too great, so that at that time the ammonia soda could not compete with the Leblanc soda even in localities where the loss of the hydrochloric acid would not have been of much consequence at that time. Apparently, about 1860, nobody manufactured ammonia soda, and the failure of all previous attempts in that direction had evidently discouraged nearly all chemists.

It was reserved to Ernest Solvay, of Brussels, to find the solution of that long-pursued problem. His first patent dates from 1861, but the process as we know it now is first described in his English patent of September 12, 1863, followed by many others in 1872, 1876, 1879, and later on. His works at Couillet, in Belgium, were started in 1863, and soda made there was exhibited in Paris in 1867 without exciting much attention. But since 1872 his triumph was assured, and has given rise to a host of other inventions, most of which have again passed into oblivion, while a few have stood the test of practice; so that ammonia soda is now manufactured not merely by Solvay's processes (which certainly furnish the largest share), but by several other independent and partly secret processes.

The reactions on which the ammonia soda process is based are the following:

(1) $NaCl+NH_3+CO_2+H_2O=NaHCO_3+NH_4Cl$;
(2) $2NH_4Cl+Ca(OH)_2=2NH_3+CaCl_2+2H_2O$;

that is, sodium chloride is treated with ammonium bicarbonate, either directly or indirectly, in successive stages—namely, first by ammonia and then by carbonic acid. If this treatment takes place at a low temperature, it leads to the precipitation of sodium bicarbonate, this salt being sparingly soluble in a solution of ammonium chloride. From sodium bicarbonate the normal carbonate can be obtained by heating. The mother-liquor, containing ammonium chloride, is treated with caustic lime, and the ammonia is thus recovered, calcium chloride remaining behind as a waste, but inoffensive, product.

Simple as this statement appears, a great amount of research has been devoted to working out the theory of the reactions.

From the nature of the case much of this work has not been made generally known, and is not, therefore, available, but the following names and references indicate a large part of what has been published. Alex. Bauer, Ber. 1874, 292; Grünsburg, *ibid.* 1874, 644; Honigman, quoted by Landolt in A. W. Hofmann's Vienna Exhibition Report, 1875, 1, 452; Schreib, Zeitsch. angew. Chem. 1888, 283; 1889, 445, 485; Bodländer and Bruell, *ibid.* 1901, 381, 405; M'Coy, Amer. Chem. J. 1903, 29, 437; Hs. Jüptner, Oest. Chem. Zeit. 1904, 247; Fedotieft, Zeitsch. physikal. Chem. 1904, 49, 2; Oest. Chem. Zeit. 67; Jäneske, Zeitsch. angew. Chem. 1907, 1559; Meyerhoffer, Verh. Gewerbst, 1905, 167; Colson, J. Soc. Chem. Ind. 1910, 186).

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[1] Ann. Chim. Phys. 1868, 64, 1.

The work done has practically all been from the point of view of the physical chemist, and consists in attempts partly experimental and partly in purely theoretical applications of the so-called 'Phase Rule,' to determine the conditions of concentration and of temperature under which the reversible reaction

$$NaCl+NH_4HCO_3 \rightleftarrows NaHCO_3+NH_4Cl$$

is most complete.

These conditions are in practice liable to modification from the practical necessity of obtaining the precipitate of sodium bicarbonate in such physical condition that it leaves the carbonators readily and can be efficiently washed.

The reactions of the process are as follows :—

1. The manufacture of caustic lime

$$CaCO_3=CaO+CO_2.$$

2. The production of ammoniacal brine by solution of ammonia in saturated brine.

3. The carbonation of ammoniacal brine

$$2NaCl+2NH_3+2H_2O+2CO_2 =2NaHCO_3+2NH_4Cl.$$

4. The calcination of bicarbonate

$$2NaHCO_3=Na_2CO_3+H_2O+CO_2.$$

5. The regeneration of ammonia

$$2NH_4Cl+CaO=CaCl_2+H_2O+2NH_3.$$

The total cycle of operations is the resultant, *i.e.* the algebraic sum of all the foregoing reactions, and it can be summed up in the following equation :—

$$\underset{\text{(Solid)}}{CaCO_3}+\underset{\text{(Dissolved)}}{2NaCl}=\underset{\text{(Solid)}}{Na_2CO_3}+\underset{\text{(Dissolved)}}{CaCl_2}-5200 \text{ Cal.}$$

Practically, however, the whole cycle of operations cannot be considered together, but each of the five stages or reactions has thermally to stand alone, and not one can be technically performed without consumption of fuel.

Equation 3, representing the actual central reaction of the ammonia soda process, is thermally almost a balance.

$$\begin{array}{ccc} (NaCl)+(NH_4HCO_3) & = & (NaHCO_3)+(NH_4Cl) \\ 96{\cdot}2+205{\cdot}6 & & 227+72{\cdot}7 \\ 301{\cdot}8 & & 299{\cdot}7 \end{array}$$

The equation represents, therefore, a typical case of a reversible reaction, and the amount of change of sodium chloride into sodium bicarbonate depends on the relative quantities or active masses of the four salts.

For instance, Bradburn (J. Soc. Chem. Ind. 1896, 882) succeeded by a ten-hours' treatment with a current of air at 21°C. in clearing a sample of 'Tower liquor' filled with suspended sodium bicarbonate, *i.e.* the sodium bicarbonate had been completely reconverted into sodium chloride by the ammonium chloride in the liquor, and the ammonium carbonate formed had been carried away by the air. This demonstrates the importance of the presence of excess of ammonium carbonate to protect by 'mass' action the sodium bicarbonate from decomposition by ammonium chloride.

Another determining factor in directing the course of interaction between the four salts $NaCl$, NH_4HCO_3, $NaHCO_3$, and NH_4Cl, is temperature. A moderate reduction of temperature, by favouring the precipitation of sodium bicarbonate, and therefore its removal from reaction, increases, in accordance with the theory of mass action, the formation of sodium bicarbonate.

A rise in temperature or a reduction of pressure by increasing the volatilisation of the only volatile member of the group, ammonium bicarbonate, tends to decrease the amount of sodium chloride converted in sodium bicarbonate.

The situation is, however, complicated by the phenomenon that by too great a reduction in temperature ammonium bicarbonate is thrown down with the sodium bicarbonate, and also that too low a temperature produces an unfavourable physical condition of the sodium bicarbonate precipitate, which makes the subsequent washing process in extreme cases practically unworkable. These facts limit the possible reduction of temperature within a small range, and nothing remains but to promote the conversion of sodium chloride into sodium bicarbonate by influence of mass action, which is in practice effected by working with a considerable excess of sodium chloride and ammonium bicarbonate, assisted by the sparing solubility of sodium bicarbonate in strong solution of sodium chloride.

This fact emphasises the importance of working the process with a sodium chloride solution as concentrated as possible.

The process.—The general nature of the ammonia soda process, and such theoretical considerations as are given above, are well known, and have been public knowledge for a considerable time. The actual working conditions in the successful ammonia soda works have, however, been kept to a large extent secret. A great number of patents, almost entirely for apparatus, have been taken out, but which are actually used, and with what modifications on the patent specification description, it is impossible to say.

Generally speaking, success in this process depends, subject to careful working in accordance with the theory of the reaction outlined above, on absolute regularity in work, and on the perfection of, and accurate interworking of the mechanical arrangements used, for the different stages of the process.

It is, in fact, the development of the mechanical and apparatus side of the ammonia soda process which converted the failure of the older workers and the pioneers of the process into the success of to-day's great industry.

We give below, however, as far as is public knowledge, the working details and apparatus used.

The raw materials required are, of course, salt (NaCl), limestone, ammonia, and fuel.

Salt. From the considerations detailed above it is clear that more than the theoretical quantity of sodium chloride is required. The actual excess of sodium chloride over that theoretically equivalent to the sodium carbonate produced is 30–40 p.c. If the sodium chloride has to be used as rock-salt, and conveyed any considerable distance, the charge for salt per ton of ash produced becomes an extremely serious item.

In practice, therefore, the chief factories for producing ammonia alkali have been established on sites where the factory can pump its own salt as a saturated brine from salt beds in its neighbourhood, or can receive its supplies of brine through a pipe line.

When the brine is pumped direct by the factory itself the actual cost per ton of salt so raised may be as low as 6*d*. per ton (*see* Lunge, Sulphuric Acid and Alkali, iii. 35).

Brines vary in composition within wide limits, but according to Bradburn (J. Soc. Chem. Ind. 1896, 880), 'A good brine for the ammonia soda process should contain about 300 grms. sodium chloride per litre, and as little as possible of lime and magnesia. Of these the magnesia is the more troublesome.'

Bradburn gives the following analyses:—

—	A good brine. Grms. per litre	Cheshire brine. Grms. per litre	New York brine. Grms. per litre
$NaCl$ . .	298·0	295·0	298·0
$CaSO_4$ . .	4·0	5·0	4·4
$CaCl_2$ . .	1·0	0·93	2·35
$MgCl_2$ . .	0·3	2·6	0·65

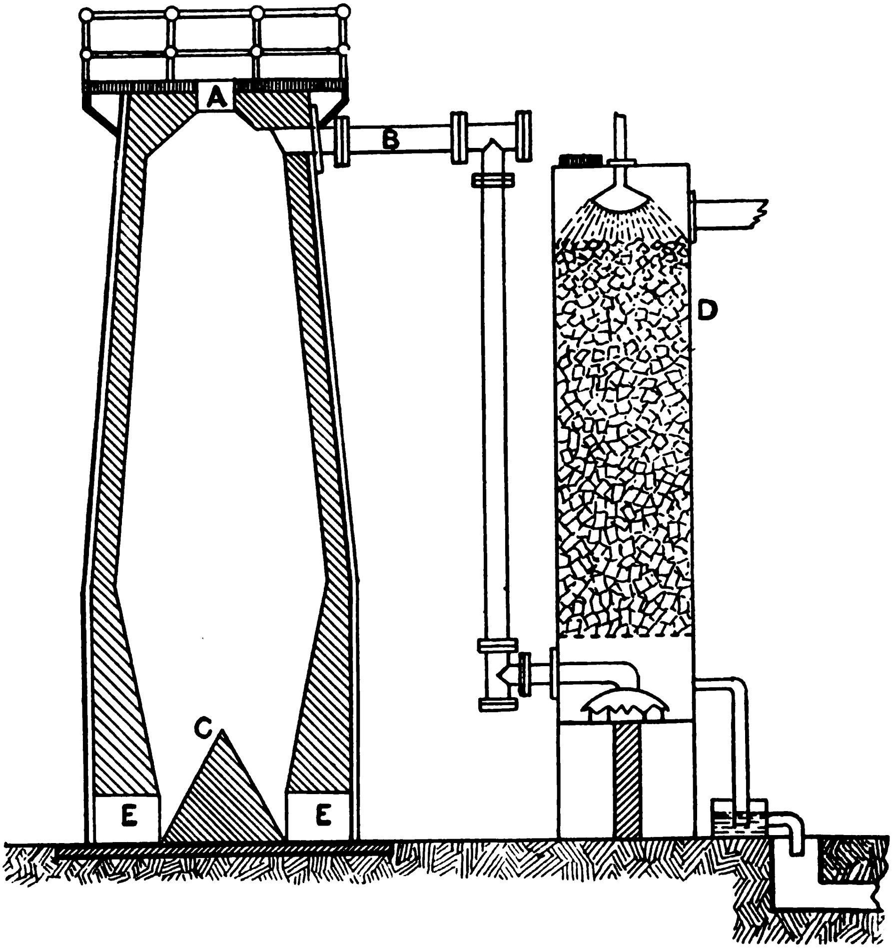


FIG. 53.

Limestone. The quantity of limestone used by the process is in considerable excess of that theoretically required and amounts to 20–24 cwts. per ton of soda ash. It is therefore of considerable importance that the ammonia soda factory should, if possible, be within a short distance of quarries of a clean limestone free from clay and low in magnesium carbonate.

We will take the actual processes in the order of the equations given in the early part of this article.

Process 1. The manufacture of caustic lime: $CaCO_3 = CaO + CO_2$.

The limestone is invariably burnt by heating with coke in tall vertical kilns.

The limestone, usually broken into comparatively small pieces, together with the necessary quantity of coke, is charged into the top of the kiln, and the burnt lime is drawn out from the bottom.

Figs. 53 and 54 represent types of lime kilns.

The kilns vary considerably in size, but are usually 30–40 ft. high and 7–10 ft. diameter.

In Fig. 53 A is the charging hole through which the limestone and coke are dropped into the kiln. The evenness with which the comparatively small quantity of coke is mixed with the larger quantity of limestone plays a very important part in determining the extent to which the quantity of coke can be reduced, and consequently the strength of the carbon dioxide obtainable in the gases.

It is necessary, therefore, to pay continual attention to this important point.

The burnt lime is drawn out through a number of openings at the base of the kiln, of which E, E are two, and through which the air required for the combustion of the coke enters the kiln.

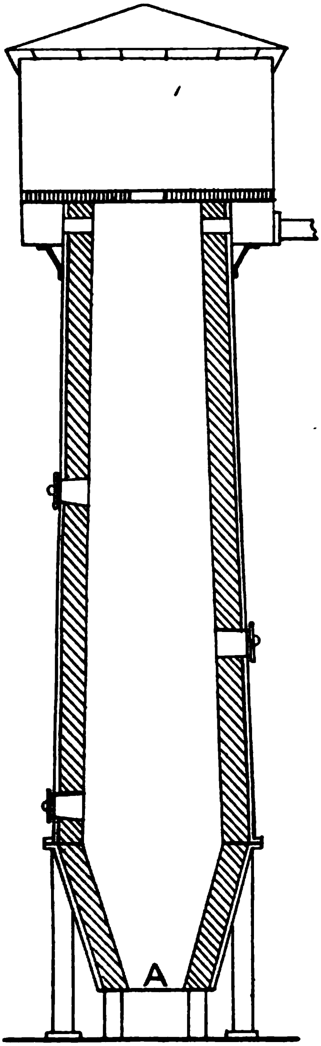


Fig. 54.

C is a brickwork cone called a 'dumpling,' which serves to prevent the accumulation of dust in the centre of the kiln, where it could not be got at for removal, and which assists in the distribution of the air to the centre of the kiln.

B is the gas exit pipe connecting the kiln to the coke packed scrubber D, of which there are usually at least two in series to each lime kiln.

Fig. 54 represents another type of kiln in which the charge is usually supported by iron bars at A, and from which the burnt lime is allowed to fall from time to time either on to the ground or into a bogie placed underneath to receive it.

According to Lunge such kilns as those described above will burn 200–300 tons of limestone a week.

The important point in lime kiln work for the ammonia soda process is to obtain as high a percentage of carbon dioxide in the gases leaving the kiln as possible, combined with a reasonably well burnt lime.

The percentage of carbon dioxide depends on the quantity of coke used, because the carbon dioxide evolved by the limestone on heating is mixed with the products of combustion from the coke, which contain only 20 p.c. carbon dioxide. Hence the smaller the quantity of coke the higher the strength of the kiln gas. The following calculated figures show approximately the relation between the coke used and the percentage of carbon dioxide.

Kiln gas strength	Cwts. coke per ton lime
31 p.c. . .	6 cwts. coke
35 p.c. . .	4·5 ,, ,,
40 p.c. . .	3·0 ,, ,,

These figures assume that the limestone is completely burnt, and the gases contain neither oxygen nor carbon monoxide, which is never the case in actual work.

The great object being to conserve heat the kiln is worked as far as possible on the regenerative principle. The cold air entering the bottom of the kiln is heated by the burnt lime as it drops from the zone of maximum temperature to the bottom of the kiln, and the hot gases, as they rise above the combustion zone, yield their heat to the cold limestone and coke freshly charged into the top of the kiln.

Radiation losses are kept within reasonable limits by the thickness and construction of the kiln walls, and are materially reduced, of course, by a high speed of work.

The actual figures published for the strength of the carbon dioxide obtained in various factories vary within wide limits.

Chance (J. Soc. Chem. Ind.) gives for good work an average test of 30 p.c. carbon dioxide. Jurisch in Chemische Industrie, 1910, 392, gives the average strength as 30–31 p.c. Again in other factories for many years an average strength of 32–33 p.c. has been obtained. Lunge describes in Sulphuric Acid and Alkali, vol. iii. 65, the Khern lime kiln, improved by Faber, which is much used in the German sugar works (Centr. für Zucker fabr. 1901, 532), and which is stated to require 5 to 7 p.c. only of coke on the weight of limestone, and to give a gas containing 40 p.c. carbon dioxide. This is a high test, but, as no aid is afforded by theory to tell us what is the highest percentage of carbon dioxide obtainable in lime kiln gases, still higher tests may be possible.

The lime kiln gases after leaving the lime kiln require to be cooled and well scrubbed to remove dust, tarry material, and sulphurous acid, as completely as possible.

A common form of scrubbing plant is two or more coke-packed wrought- or cast-iron towers, about 30 ft. high by 5–8 ft. diameter, connected in series and down which a stream of water is run.

The lime drawn from the bottom of the kilns should be well burnt. Whatever calcium carbonate is left unburnt is, however, recovered in the lime pot, and is returned and charged a second time into the kiln with the fresh limestone. A factory producing 500 tons ammonia soda a week would require three such kilns as those described.

2. *The production of ammoniacal brine.* As mentioned above, the impurities in the brine, viz. the lime and magnesia salts, are a source of trouble in the pipes and connections unless previously removed. In practically all cases now this purification takes place simultaneously with the absorption of ammonium carbonate which throws down the lime salts. The purification has been done as a separate process by the addition of sodium carbonate and lime, but that is not the general practice. Occasionally the soda crusts from the cleaning of the towers and sweeping of dirty soda from the floors are used, but as a rule the purification is done as stated above by the ammonium carbonate in the ammonia used for ammoniating the brine, and the scales produced by the hard crystalline magnesium salts are mechanically cleaned from the pipes and connections at intervals.

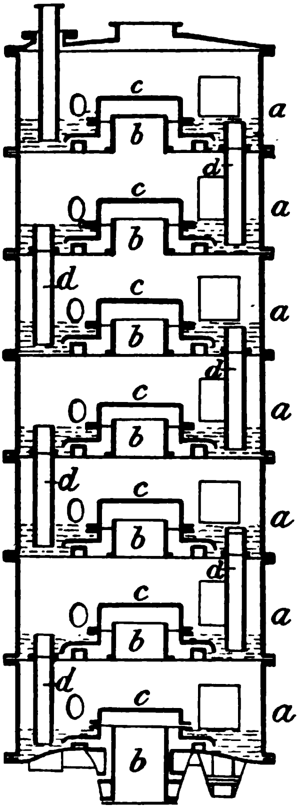


FIG. 55.

The fresh brine entering the works goes into a vessel called a tower washer where it serves to scrub the ammonium carbonate mechanically carried over from a battery of Solvay towers.

A common type of tower washer is shown in Fig. 55 which consists of a series of cast-iron rings *a, a,* &c., divided by plates with central holes *b, b,* &c., covered with a cup or mushroom *c, c, c,* &c., which has serrated edges and often is perforated with small holes. The brine running down the tower accumulates on each plate until it is sufficiently deep to run down the overflow pipe *d, d, d,* &c., to the shelf below. The gases travelling upwards pass through the central hole of each shelf under the mushroom, and then bubble out round the serrated edge through the brine. The fresh brine entering the top of the tower naturally meets the gases from which the ammonia has practically all been absorbed. This system of bringing gases and liquids into contact in towers divided into compartments by a number of shelves with a central hole for the passage of the gases covered with a mushroom, the serrated edges of which are luted with the liquor, is characteristic of the Solvay ammonia soda process, and is used in various parts of the process. It is the same idea as that in the Coffey's still for the distillation of alcohol. The lime in the brine is to a large extent precipitated in the tower washer by the ammonium carbonate absorbed. The calcium carbonate does not, however, settle out, but remains in suspension in the liquor agitated by the current of gas and travels on with the brine through the ammonia absorber or ammoniating vat to the vats or store tanks where it settles out.

In consequence of the calcium carbonate remaining in suspension the tower washer runs for many months without necessity for cleaning. From the tower washer the brine runs into the ammonia absorber or ammoniating vat, in which the brine is saturated with ammonia from the stills.

The ammonia absorber is usually a cast-iron vessel made up of three or more cast-iron rings similar in principle to the tower washer just described. Fig. 56 shows one type of absorber: *a, a, a,* are the shelves, *b, b, b,* mushrooms, as described in the case of the tower washer, *c, c, c,* the pipes through which the liquor overflows from each shelf to the one below.

The bottom of the absorber is conical and is fitted with a discharge pipe and tap through which the sludge that settles out may from time to time be drawn. Another type of absorber is shown in Fig. 57, and is a vessel built up of several cast-iron rings, frequently about 8 ft. diameter, but without the shelves shown in Fig. 56. In this case the gases enter by the pipe A, and are distributed by the single mushroom B. The bottom of the vessel again is conical to permit the occasional blowing off of slurry. The ammoniacal gases from the stills are drawn through the absorber by a vacuum pump, which, as a check on ammonia escape, sends on the gases it has exhausted through an additional small tower or washer generally called the vat washer. The vat washer usually receives the brine coming from the tower washer and only in very exceptional cases is fed by fresh brine. By using the tower washer brine a natural and continuous circuit is established for the flow of the brine through the process.

Heat is generated in considerable quantities in the absorber by the solution of ammonia and cooling is necessary. This is done either by an external spraying with water or preferably by internal cooling pipes.

The ammoniacal brine should be cooled in the absorbers, and should not at any rate exceed 30°C.

The gases, however, entering the absorbers from the stills should be maintained at about 70° in order to prevent blockages of the ammonia main by the formation of ammonium carbonate crystals.

Deposits of ammonium carbonate and of carbamide are thrown down and block up the pipes and connections. It is, therefore, a very difficult matter to reduce the steam in these gases to a low enough point to avoid excessive dilution of the brine. At the best these gases can only enter the brine saturated with moisture at 70°–75°.

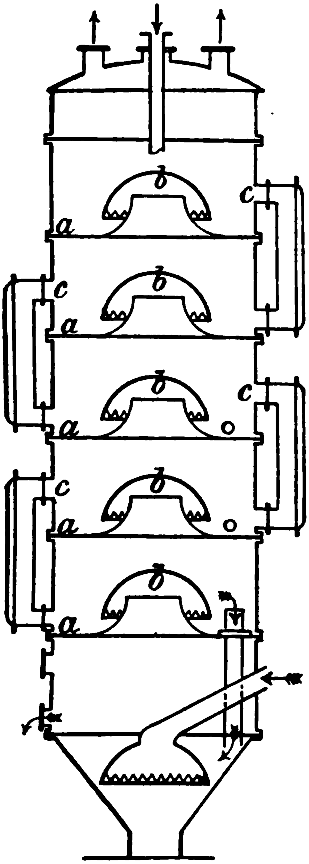


Fig. 56.

Naturally the strength of the brine solution is a very important point. The output of the plant depends on it.

A good saturated ammoniacal brine should contain 27–28 p.c. sodium chloride and 6–7·5 p.c. ammonia. The theoretical equivalent of 27 sodium chloride is 7·8 ammonia, so that nearly equal equivalents are used. The following figures, determined experimentally by Schreib, indicate the variation in the completeness of the carbonation reaction with the variation in the proportion of $NH_3 : NaCl$.

Original solution		Carbonated solution				
P.c. NH_3	P.c. NaCl	P.c. NH_3	P.c. NaCl	P.c. NH_4Cl	P.c. decomposition	Grams Na_2CO_3 per litre
3·4	29·6	0·6	20·1	9·1	33·1	90
6·6	27·3	1·3	10·2	16·1	63·1	146
7·2	27·2	1·3	9·3	17·9	67·8	154
8·9	25·8	1·3	7·4	18·8	73·6	168
13·2	23·5	2·9	9·5	14·2	62·0	132

The large scale results are not identical with the laboratory results, which are comparative only between themselves.

The large scale decomposition with the normal ammoniacal brine given above should exceed the maximum figures given by Schrieb, and is stated to vary between 73 and 78 p.c.

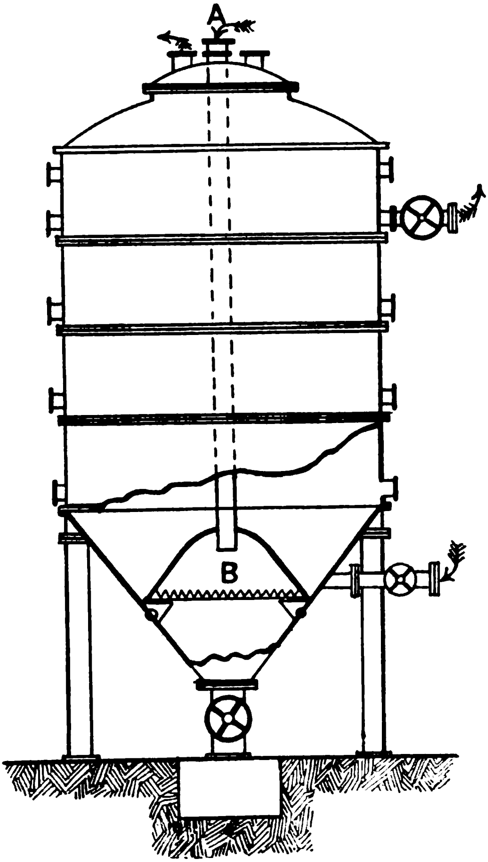


Fig. 57.

The presence of ammonia and ammonium carbonate decreases the solubility of sodium chloride in water.

Lunge gives the following figures for the solubility of sodium chloride in water in the presence of ammonia at 15°.

P.c. NH_3 by vol.	P.c. NaCl by vol.
—	31·78
3·5	29·5
5·0	28·6
6·0	28·0
6·5	27·7
7·0	27·4
7·5	27·1
8·0	26·8
10·0	25·4
12·0	24·1

The bulk of a brine solution on addition of the 6–7½ p.c. ammonia required for the carbonation process increases by 9 p.c.

From the absorber the ammoniacal brine runs in a continuous stream into the 'vats.'

The vats are frequently cast-iron vessels built up in four rings on a cone-shaped bottom piece supported on columns exactly similar to the vessel shown in Fig. 57 without the gas delivery pipe A and mushroom B. A common arrangement is for the ammoniacal brine to run in a continuous stream through two of these vessels in series and from there into one or other of two more similar vessels which act as measuring tanks, one being emptied while the other is filling. The mud, consisting chiefly of calcium carbonate mixed with a considerable proportion of ferrous carbonate and hydrate, settles out mainly in the two leading vats and is drawn off through the discharge pipes at the bottom of the cones at regular intervals. A further but small quantity of mud settles out in the measuring vats.

The mud is usually mixed with other liquors (from the filters, for instance), and pumped to the ammonia stills where the ammonia carried away with the liquid in the mud is recovered.

The 'tower washer,' ammoniating plant, 'absorber' and vats are usually erected at such heights that the brine from the 'tower washer' will flow by gravity into the 'absorber' and then on to the 'vats.' In this way the brine is only pumped once. The absorber, vats and ammonia still are usually all included in the same vacuum circuit, the exhaust gases from which pass through the vat washer or final small scrubber mentioned above to ensure recovery of all ammonia.

As has been mentioned, dilution of the brine is bound to take place to some extent through the uncondensed steam entering the absorbers with the gases from the stills.

It was formerly the custom to make good this dilution by the addition of solid sodium chloride in the carbonating tower itself. This, however, is generally discontinued and either the cooled ammoniated brine is strengthened by passing through a separate closed vessel containing salt, on its way from the coolers to the carbonating towers, or it is pumped direct to the carbonating towers at the strength at which it leaves the absorbers.

The well-settled ammoniacal brine has now to be cooled as far as possible before being carbonated, and this is generally done in a series of 6-inch cast-iron pipes arranged in tiers one above the other. The pipes are either submerged in a water tank or cooled by a stream of cold water flowing down and over them. The coolers are arranged in pairs or trios so as to permit of cutting out a cooler for cleaning. For instance, if there is a set of three coolers, two of them will at any time be working, the third will be disconnected for cleaning. Very troublesome crusts are formed in these coolers, which have first to be steamed to soften them and then chipped out.

Reinitzer (Zeitsch. angew. Chem. 1893, 446) gives the composition of these crusts as Na_2CO_3, $MgCO_3$, NaCl. Pennoch, Chem. Trade Journal, 1893, 191, found crusts in the coolers of the composition $MgCO_3$, Na_2CO_3.

In the great majority of the ammonia soda works the central reaction of the process, viz. the carbonation of the settled cooled ammoniated brine is carried out in a tower originally designed by Solvay (patented in 1872), and which is therefore called the 'Solvay Tower,' and is the most important apparatus in the process.

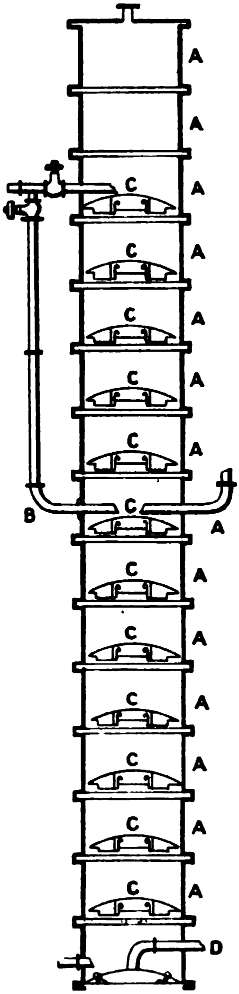


FIG. 58.

Fig. 58 represents a Solvay tower, which consists of a number of cast-iron cylinders A, A, &c., approximately 3 ft. 4 ins. deep by 5 ft. to 8 ft. diameter. The bottom of each cylinder is formed by a cast-iron disc with a central opening not shown in the drawing, about 1 ft. 4 in. diameter. Over the opening is supported a perforated cover C, C, &c. (shown in detail, Fig. 59), about 6 inches less in diameter than the cylinder itself. The actual number of these cylinders in a tower varies usually between 15 to 25 with the practice of the different factories.

The ammoniated brine enters the tower by the pipe B under pressure, and is maintained at a level 6 ft. to 10 ft. from the top of the tower. The object of feeding the fresh liquor part way down the tower, to which Solvay attaches great importance, is to avoid excessive volatilisation of ammonia, which if driven out of the tower is, of course, useless for the reaction.

The carbon dioxide gases from the lime kiln, enriched, as will be described later, by the carbon dioxide obtained from the first roasting of the bicarbonate, are compressed to sufficient pressure (varying with the height of the towers from 1½ to 2½ atmospheres) to overcome the resistance of the Solvay tower and the subsequent washers, and enter the tower through the pipe D. A constant feed of ammoniated brine is pumped into the tower at B, and a constant stream of carbon dioxide is pumped into the bottom of the tower at D.

The gases travelling up through the openings in the bottom plates of the cylinders are split up by the perforated covers, and, part passing through the perforation in the mushrooms, and part bubbling round the edges of the mushrooms, come in a comparatively fine state of division in contact with the liquid in the tower. With the assistance of the constant agitation the stream of ammoniated brine carries down with it practically all the bicarbonate precipitated from it.

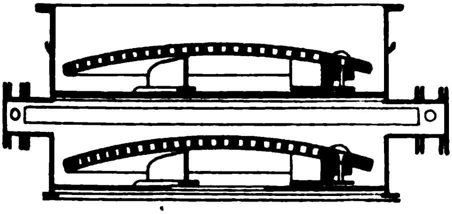


FIG. 59.

The increased partial pressure of carbon dioxide in the gases at the bottom of the tower, due to the pressure, increases the speed of the reaction.

One of the most important technical points in the working of the Solvay towers is, as indicated above, the regulation of temperature. The absorption of carbon dioxide by aqueous ammonia liberates considerable quantities of heat, the larger part of which is produced in the formation of the mono-carbonate $(NH_4)_2CO_3$.

To avoid this, in some cases a supplementary Solvay tower has been added in which the greater part of the mono-carbonate is produced.

In other cases part, or the whole of the ammonia (NH_3) is mono-carbonated in an intermediate vessel of the type of a tower washer placed between the ammonia vats and the feed pump to the Solvay towers, and which is supplied independently with carbon dioxide from the lime kiln.

Bradburn thus describes the working of a Solvay tower.

'It was stated that the carbonating of the vat liquor is made only nearly complete: this is of course completed in the carbonating tower. In the upper rings, where the liquor is warmer, the crystals of bicarbonate of soda begin to form; if the tower is cooled too much a small, fine-grained, muddy bicarbonate is made which is very difficult to wash free from salt, and which is very difficult to dry. On the other hand, if the liquor is not cooled enough the production is diminished. But at a certain temperature and point in the tower for this temperature, both found by experience, a coarse-grained bicarbonate is obtained, which washes quickly and well, and which when taken from the filters and crushed in the hand no water is squeezed out of it; this kind dries in calciners without forming balls the outside of which is ash and the core bicarbonate. The temperature of the gas going to the tower runs about 28°. The pressure on the gas runs about 55 inches of mercury at the bottom, and about 9 inches at the top; the top pressure is due to the liquor in the tower washer. When ordinary vat liquor of 39 to 40 grms. CO_2 per litre is fed into a tower there is more ammonia carried off by the unabsorbed gas than when liquor of 69 to 70 grms. CO_2 is used.

'Each cubic metre of waste gas carries away about 112 grms. of NH_3 when 40 grms. CO_2 liquor is used, against 58 grms. carried off when using 70 grm. CO_2 liquor. The quantity of bicarbonate suspended in the liquor increases, of course, as the liquor travels down the tower. If a sample of liquor be taken from the bottom it will be found after standing about half an hour that the volume of the bicarbonate is from a quarter to a third of the total volume of the sample.'

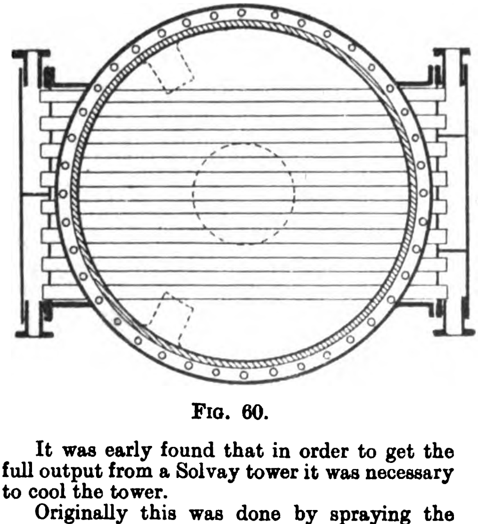


FIG. 60.

It was early found that in order to get the full output from a Solvay tower it was necessary to cool the tower.

Originally this was done by spraying the exterior of the tower with water. This is naturally an inefficient method, and is not capable of satisfactory regulation. Cogswell (Eng. Pat. 1973 of 1887) applied a system of internal cooling pipes, Figs. 59 and 60, in the tower cylinders;

cooling water is circulated through the pipes and enables the temperature to be regulated in the different parts of the tower.

The top of the tower should be kept as cool as possible to avoid volatilisation of ammonia, and the middle and lower parts should be maintained at a temperature of about 20°, as steadily as possible.

Cleaning the Solvay tower. The Solvay tower normally runs two to three months without blocking up and requiring cleaning.

The tower is cleaned by first of all emptying out the liquor in it, maintaining the usual agitation by pumping in kiln gas while the liquor runs out. Water is then run into the tower, and the whole boiled up with steam. This dissolves out the soda crusts that have been formed.

Other forms of carbonators. Numerous other forms of carbonators have been suggested, and some are worked on the large scale.

As, however, the Solvay tower is, with a few exceptions, the apparatus universally employed, only a list of the more important alternatives are given here.

Of the vertical type. Schreib, D. R. P. 70169; Honigmann, D. R. P. 13782; Schreib, Chem. Zeit. 1890, 492.

Of the horizontal type. One of the oldest apparatus is that of Gossage (Eng. Pat. 422, 1854; Young, Eng. Pat. 2558, 1871).

The Boulouvard apparatus, which has been employed successfully in France, is described in Fr. Pat. 125625, 1878; Pechiney, Eng. Pats. 2098 and 5394, 1880, describes a modification of the Boulouvard apparatus.

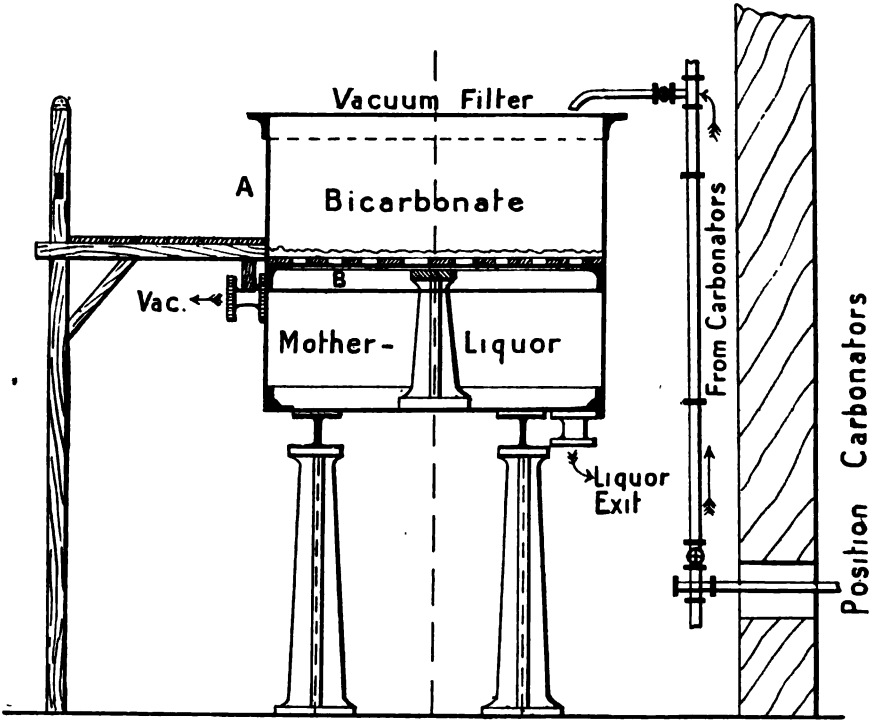


FIG. 61.

Filtering the precipitated bicarbonate from the Solvay tower liquor. Fig. 61 represents a common form of filter. The shell A is of steel plates, varying in size up to 12 ft. diameter. The filter bed B usually consists of a perforated cast-iron plate on which rests a coarse flannel filter cloth, over which is a wire mesh grid to protect the flannel from the spade used to empty the bicarbonate from the filter. A series of five such filters are connected to a battery of four Solvay towers, and are alternately filled with the liquor and salts flowing from it.

While filling, the space below the filter bed is placed under vacuum, and receives the filtered liquor. When the bed of bicarbonate on the filter has become about 24–28 ins. thick, the stream of liquor is turned on to another filter. As soon as the mother liquor has been drawn through the salts, the surface of the salt is smoothed over and any cracks, especially round the edges of the vessel, made good. The salts are then washed with water, delivered by a spray, until the chloride in the bicarbonate has been reduced to 0·1–0·2 p.c. NaCl.

When this is done the spray of wash water is stopped, and the vacuum maintained until the bicarbonate is drained as dry as possible. The usual rough test with a normal good grain bicarbonate is that a ball of the salts when pressed in the hand does not yield water.

Bradburn gives the following analysis of the washed bicarbonate:—

$NaHCO_3$	70–75	p.c.
Na_2CO_3	3–5	,,
NaCl	0·2–0·7	,,
NH_3	0·56	,,
H_2O	24–25	,,

It is practically impossible to wash the precipitated bicarbonate free from ammonia or sodium chloride without an altogether extravagant loss of bicarbonate.

As it is, the washing results in a material loss of bicarbonate.

The efficiency of the washing operation depends more upon the physical condition of the bicarbonate itself than upon apparatus. This physical condition, as described above, depends on the temperature conditions of the Solvay tower.

At low temperatures in the tower not only is the precipitate in a very fine state of division, and practically impossible to wash, but it contains ammonium chloride in the solid state, which experience has shown is with the utmost difficulty taken up by the wash water.

The mother liquor and wash liquor after the removal of the vacuum under the filter are run off into the store tanks or wells, from which they are afterwards pumped to the ammonia stills.

Several mechanical filters have been devised which permit of continuous and automatic filtering, washing, drying, and removal from the filter bed, thus effecting a material saving in labour.

Figs. 62 and 63 represent the filter patented by Solvay (4725, 1896), in which A is a drum revolving in the vessel B into which the liquor and salts from the towers are fed, and in which they are kept agitated.

The drum A revolves about a horizontal hollow axle C connected with a vacuum pump. The periphery of the drum A is formed of a perforated metal sheet, covered with a fine metallic cloth in which a piece of flannel is secured. As the drum revolves the internal suction draws in liquor and forms a coating of bicarbonate on the surface.

In order to prevent the pores of the filtering bed becoming clogged, internal pressure is substituted for the vacuum from time to time.

The cake of bicarbonate as it travels round is sprayed with water and is effectively washed at a later stage of the revolution, the vacuum drys the thin cake of bicarbonate, after which it is continuously removed by a scraper.

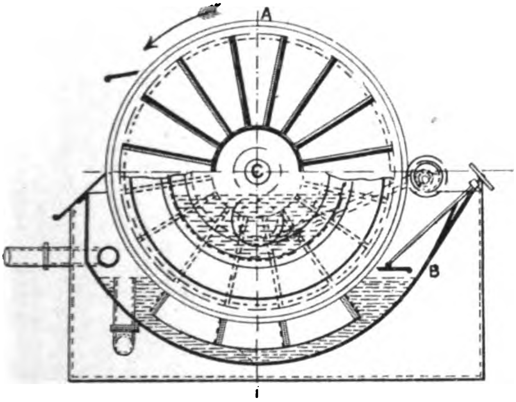


FIG. 62.

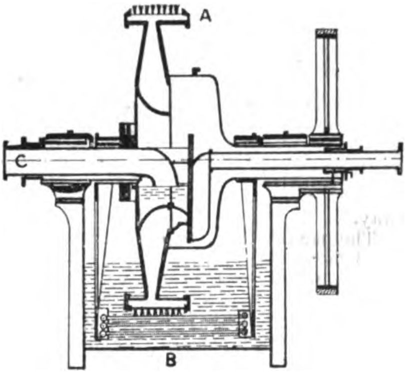


FIG. 63.

Another mechanical filter is described in Eng. Pats. 7957 and 28791, 1903, taken out by Houghton and the United Alkali Co., Ltd.

This filter consists of an inclined rotating dish provided with a false bottom of filtering material. The dish is divided into compartments below the filter bed, which are alternately in communication with the suction device to carry away filtrate, and with a supply of mother liquor or water to wash the solid matter from the pores of the filtering material. A stream of liquor and salts from tower is run on to the rotating filter bed, the liquor passes through, drawn by the suction, and the bicarbonate is left as a comparatively thin layer, which in the course of revolution of the dish is washed by a water spray and then automatically removed by a scraper or plough.

From the filters the washed and drained bicarbonate is taken to the roasters or furnaces to be converted into the monocarbonate or soda-ash. From the ordinary filters of the type shown in Fig. 61 the bicarbonate is discharged by hand into barrows or trollies, in which it is conveyed to the roasters.

From the mechanical filters the bicarbonate, as it is continuously removed by the plough, is carried away by a conveyor and fed continuously into the roaster.

The roasting and furnacing operation. From the readiness with which sodium bicarbonate decomposes it would be anticipated that the roasting and furnacing operation would be an easy matter. Practically it has been found that the economical performance of this operation is one of the most difficult problems in the process.

The difficulty is indicated by the large number of patents on this part of the process taken out by Solvay and others.

The practice in the various works is understood to vary widely, and the details of the apparatus in actual use are, as is the case with so much of this process, kept secret.

Below are given short descriptions of some of the furnaces which have been used.

It is usual to divide the calcining operation into two stages. In the first, the bicarbonate is dried and the ammonia contained is driven off together with about 75 p.c. of the second molecule of carbon dioxide. The product, called 'roaster ash,' is then subjected to a second calcination at a higher temperature to complete the decomposition of the bicarbonate. Fig. 64 represents a form of roaster which has been much used. It consists of a cast-iron pan A closed by a cover B through which passes a vertical shaft, carrying an arm with scrapers. The pan is heated by the fireplace C, and is provided with an exit pipe D, through which the gases evolved —steam, ammonia, and carbon dioxide—pass away.

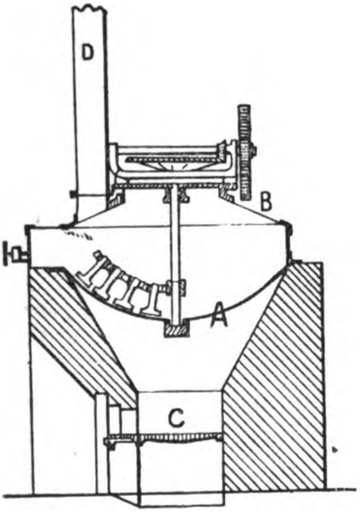


FIG. 64.

The pan of such a roaster varies in size from 10–14 feet.

Fig. 65 represents an apparatus modelled on the Thelen pan described in Die Chemische Industrie, 1878, 7, and which has been very largely used for the finishing operation where a light quality ash is wanted.

The Thelen pan consists of a cast-iron dish 7–8 ft. diameter by 30 ft. long, hooded with a sheet iron cover. The pan is heated by an external fire and rests on brick walls. The roaster ash is fed continuously at the firing end, and slowly moved by the oscillating movement of the scrapers, which rock through an angle of about 90°, to the other end of the pan, where it is delivered to a conveyor, or to an elevator, which lifts it to the so-called cooling conveyor, usually placed in the roof of the building, and from which the ash is afterwards conveyed to the store or to the dressing and packing plant.

The cooling conveyor is sometimes an atmospherically cooled revolving shell, having an inside screw fastened to the shell, and sometimes a water-cooled conveyor.

The Thelen pan as shown above, but fitted with an exit pipe near the fire end, is also used for the whole operation of drying and furnacing.

The wet bicarbonate is fed in at the fire end, and the monocarbonate delivered, as described above, from the end further from the fire into the elevator feeding the cooling conveyor. The water vapour, ammonia, and carbon dioxide escape by the exit pipe.

Bradburn (J. Soc. Chem. Ind. 1896, 884) states that in the United States the form of dryer shown in Fig. 64 is in use, but is being replaced by the calciner described in U.S.A. Pat. 386664, 1888. This calciner consists of a cast-iron cylinder about 60 ft. long by 5 ft. diameter, supported at the ends and in the middle on roller bearings, and revolved by gear fixed in the middle. A furnace chamber is built round each half of the calciner, connected together by flues. The ash is moved by means of a heavy chain lying along the length of the cylinder.

The apparatus described above yields the sodium carbonate in the form of a light powdery ash requiring very little grinding before packing, but occupying, when compared with Leblanc ash, materially more package space.

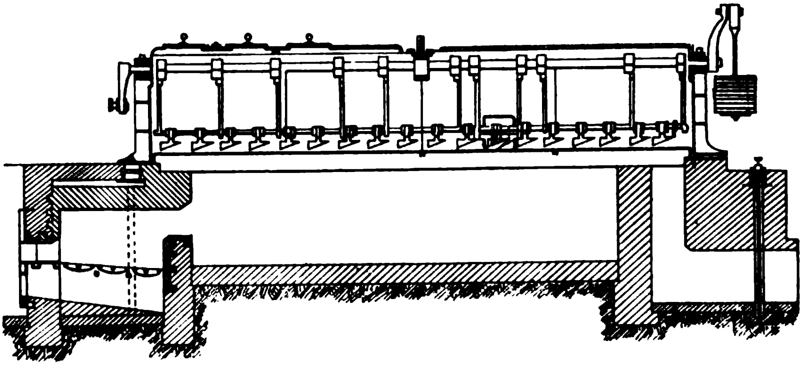


FIG. 65.

For many purposes this light, somewhat dusty ash is not liked, and a denser form has to be made by subjecting it to direct fire.

When this is done the 'roaster ash,' that is the not completely decomposed bicarbonate or sesquicarbonate, taken from either the dish roaster shown in Fig. 64 or produced in a lightly fired Thelen pan, is finished in a furnace of the type of the Mactear furnace shown in Fig. 48, p. 54, or in a rotating furnace of the type of the black ash revolver, where the ash is brought into direct contact with the fire gases, and therefore raised to a much higher temperature than in the Thelen or other similar pan.

Bradburn gives the difference between the light and heavily-finished ash as follows :—

A 1000 c.c. jar filled and well shaken down with light ash, will hold 900 to 1000 grms. weight of ash. If the ash is heavily finished, the jar will hold about 1550 grms.

As mentioned above, whatever apparatus is used for drying and roasting the bicarbonate, arrangements are made to draw off the gases (NH_3, CO_2 and H_2O) evolved.

The gases are drawn by means of a pump, first through a series of water-cooled cast-iron pipes, similar to the cooler for the ammoniacal brine, to cool them and condense the bulk of the water vapour which carries with it a part of the ammonia.

They are then usually drawn through one or more coke-packed towers, down which water is running, and in which the remainder of the ammonia is condensed as ammonium bicarbonate. The ammonia liquor both from the cooler and the scrubber is run to the store tank for ammoniacal liquor, from which the ammonia still is fed.

The gases leaving these scrubbers consist of carbon dioxide diluted by the air drawn into the roaster.

Great care is taken to reduce this air leakage to a minimum, because with absolute freedom from leakage the carbon dioxide from the roaster would, of course, test 100 p.c. CO_2, and when mixed with the lime kiln gases pumped into the Solvay towers or carbonators would materially increase their strength.

In the early days the roaster carbon dioxide tested as low as 25 p.c. With the dish roasters (Fig. 64) the carbon dioxide is stated to test about 50 p.c. With great care and the more modern roaster, such as those of the Thelen type, it is stated that a gas containing 60–80 p.c. carbon dioxide is obtained.

Ammonia recovery. The ammonia used in the process, with the exception of the unavoidable losses, is recovered by the distillation of the various ammoniacal liquors collected as described above.

The larger part of the ammonia is contained in the mother liquors from the filters, and is present mainly as ammonium chloride. Of the total ammonia going to the stills, about 15–20 p.c. is, however, present as bicarbonate, and is therefore volatile. Again, the ammonia losses are made good by the addition of fresh ammonia liquor from gas works and recovery coke ovens, which is chiefly in the form of oxide with some carbonate and sulphide. This fresh liquor is added to the general stock of filter liquor, and is fed with it into the still.

The liquors also contain, of course, the excess of sodium chloride which has passed through the Solvay towers.

Fig. 66 shows the form of still in general use. A, A, A, are compartments made of steel plates or cast-iron rings, separated by cast-iron plates, each with a large-sized hole in the centre covered by an umbrella-shaped mushroom.

B is the chamber into which the milk of lime necessary to decompose the fixed ammonia, *i.e.* such salts as the chloride which are not decomposed by heat, is run.

C, C, C, C, are a number of compartments, each consisting usually of a cast-iron ring. The bottom plate of each ring has a central hole covered with a plate.

The filter liquors are fed in at the top of the still through the pipe E, and passing down the upper part of the still or 'heater' are heated by the steam rising from the lower half, and the ammonium carbonate and bicarbonate are decomposed and driven off.

The liquor then passes into the chamber B, where it is mixed with the milk of lime pumped in through the inlet G.

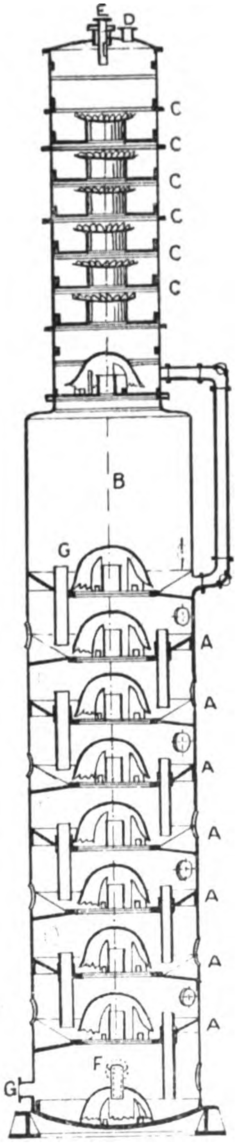


Fig. 66.

The lime decomposes the fixed ammonia, namely ammonium chloride, and any sulphate present, and in passing down through the compartments A, A, &c., the liberated ammonia is driven off by the steam which enters at F.

From the top of the still ammonia, steam, an carbon dioxide pass away through the outlet D, at a temperature of 80°–85°.

As has been stated previously, it is very important before the ammonia is brought in contact with the brine, that as much steam as possible should be condensed, and that it has been found that the gases should be cooled so that they enter the absorbers at 70°–75°.

The distiller cooler or condenser may be of various forms, but is usually a vessel built up of cast-iron rings. Near the top of the vessel, and also near the bottom, is a cast-iron tube plate, into which are expanded a number of tubes. Cooling water is circulated through these tubes, entering below the bottom tube plate and flowing away from the top. By regulating the cooling water supply, the temperature of ammoniacal gases leaving the cooler or entering the absorber is controlled. The ammoniacal liquor condensed in the cooler is either run back into the filter liquor store or into the still itself at some point in the upper or heater part of the still depending on the levels.

For the efficient working of the still itself, and for the smooth interworking of the still and the absorber, regularity is required—

1. In the test of the ammonia in the filter liquor feed. It is therefore a matter of importance to watch carefully the average strength of the liquors collected in the filter liquor store tanks.

2. In the supply of the milk of lime, which should always be in slight excess. If there is a deficiency of lime there is incomplete decomposition of the ammonium chloride, and loss of ammonia.

3. In the supply of steam, because if there is a deficiency of steam there is incomplete distillation of the ammonia, and loss in the exit liquors. If, on the other hand, there is an excess of steam, the cooler will be overworked, and the gases entering the absorber will contain an excess of water, and thus dilute the brine.

The lower parts of the stills gradually become blocked up with scale which adheres to the shell, the mushroom, and all parts of each compartment, sometimes to the thickness of three inches.

From time to time this has to be cleaned away, and the only method available is, after well steaming out the still and allowing it to cool, to chip off the scale by hand.

The scaling requires to be done every one to two months, depending on the speed of work.

The loss of ammonia in the whole process varies between ½ and 2 p.c., estimated as ammonium sulphate on the ton of soda ash made. Good ammonia results are, of course, dependent on the careful carrying out of the precautions indicated above, and have been effected only by the gradual accumulation of experience and improvement of apparatus. Bradburn says that an ammonia soda works requires to carry a stock equal to two tons of ammonium sulphate per ton of ash made per day. Of this 25 cwts. are in the form of working liquors.

The waste liquor leaving the still is a solution of calcium and sodium chlorides, containing the excess of lime mentioned above, and also calcium carbonate, due to the unburnt calcium carbonate in the lime which gets past the filters of the lime slaker, and also due to any carbon dioxide not driven off in the upper part of the still. The liquor also carries away any other impurities which may have been in the limestone.

It is the usual custom to run this liquor through settling ponds, where the lime, calcium carbonate, and other solids separate out, after which the solution of chlorides is run away.

It will be noted that the calcium chloride thus run away contains all the chlorine combined with the sodium which has been converted into sodium carbonate, and, in addition, the liquor carries away unused about 20–40 p.c. of the total salt brought into the process.

A very great amount of work has been done to try and utilise the chlorine thus lost by the ammonia soda process, but without success. See article CHLORINE, p. 43, vol. ii.

It is necessary to reiterate that success in the working of the ammonia soda process depends on the balance of the different sections of the plant, so that by careful supervision a mechanical interworking of the different parts of the process may be attained.

Application of the ammonia soda process to sodium sulphate. As the ammonia soda process starting from sodium chloride does not economically yield hydrochloric acid, attempts have been made to work the process using sodium sulphate as the starting-point.

In this case the hydrochloric acid is evolved in the production of the sodium sulphate. The process is first mentioned by Bower (Eng. Pat. 8413, 1840), and was afterwards considered by Gerlach and by Weldon (see Eng. Pat. 5605, 1883). Gaskell and Hurter were, however, the first to seriously attack the difficulties of the process (see Eng. Pats. 5712, 1883; 8804, 1884; and 9208, 1886). The great difficulty was how to deal with the ammonium sulphate formed in the reaction. Gaskell and Hurter's scheme was to heat the ammonium sulphate with sodium sulphate in a current of steam, when the ammonia is liberated and acid sodium sulphate left behind. The process then followed the three reactions—

$$(1)\ Na_2SO_4+2NH_3+2CO_2+2H_2O =2NaHCO_3+(NH_4)_2SO_4.$$

$$(2)\ (NH_4)_2SO_4+Na_2SO_4=2NH_3+2NaHSO_4.$$

$$(3)\ NaHSO_4+NaCl=Na_2SO_4+HCl.$$

The second stage of the process was, however, always the stumbling block, and, owing largely to its cost, this interesting process was not persevered with.

Application of the ammonia soda process to sodium nitrate. This was suggested in 1876 by Gerlach and patented in 1877 by Lesage & Co., and again by Chance (Eng. Pat. 5919, 1885). Colson (J. Soc. Chem. Ind. 1910, 190), again, recommends this process as being theoretically more favourable than the sodium chloride process.

Caustic soda from ammonia soda. In competition with Leblanc process, caustic soda is manufactured on a considerable scale by the makers of ammonia soda. As has been stated before, although the ammonia soda process has proved itself much the cheaper process for the manufacture of sodium carbonate, the Leblanc process, owing to the numerous bye-products produced, and to the fact that the Leblanc vat liquors are already a solution of partially causticised soda, is the better adapted for the production of caustic soda.

The manufacturers of caustic from ammonia soda either make use of Löwig's ferrite process described on p. 48, and thus produce a solution of 1·32–1·36 sp.gr. at once, or dissolve the ash in water and causticise by lime in exactly the same way, and using the same apparatus as is described above for the Leblanc vat liquors, p. 45.

Although the Löwig process has been adopted by some of the largest makers of caustic from ammonia soda, and although it possesses the double advantage of producing a stronger solution of caustic, and of avoiding the very serious trouble of finding an outlet, or depositing ground, for the large quantities of caustic lime mud produced by the lime process, it is doubtful if there is much difference in cost between the processes.

In either case the later stages of the concentration and finishing are carried on in the same way, and in the same apparatus, viz. cast-iron caustic pots, sometimes supplemented by multiple effect evaporators, such as have been already described under the Leblanc process.

To some extent ammonia ash is also causticised by consumers such as paper makers, textile bleachers, and soap makers, who require a solution of comparatively low strength caustic soda liquor in their manufacture. When actual costs are obtained, however, it is very rarely found that the production of their own caustic liquor pays when compared with price of already made caustic.

Local conditions as to prices of fuel, lime, and facilities for waste deposit vary too much to enable a standard comparison to be made, applicable to every case, but it is necessary to remember that to produce caustic liquor of 1·1–1·13 sp.gr., equivalent to 1 ton 70 p.c. caustic soda, requires from actual results in such works, 29–30 cwts. 58 p.c. soda ash, 17–18 cwts. lime, 20 cwts. fuel.

In addition to this there have to be deposited 2¼–2½ tons of caustic lime mud, and the wages, repair and capital charges to be met. The soda liquor obtained in this way contains about 90 p.c. of its total soda only as hydroxide, the remainder as carbonate, and if great care is not exercised in the washing of the lime mud on the filters before sending to the tip, the soda losses may be largely increased.

Soda crystals. For some purposes soda is required not in the calcined form, as soda ash, but in the crystalline form, in which it contains 10 molecules of water. Although soda crystals, if chemically pure, contain only 37·08 p.c. of anhydrous sodium carbonate, or 21·71 p.c. of available soda (Na_2O), and thus cost much more than their equivalent of soda ash for packages and carriage, they are preferred to the latter in some cases, for the following reasons: while soda ash is a more or less white powder, whose value cannot be recognised at a glance, and which may contain more or less useless, or even injurious, impurities, soda crystals by their very appearance seem to guarantee to the buyer a product of sufficient purity and of uniform strength. Their greatest recommendation for household use, as well as for the scouring of wool and some other purposes, is their absolute freedom from caustic, which is very injurious both to the skin and to the fabrics to be washed or scoured. For all manufacturing purposes soda crystals are now advantageously replaced by ammonia-soda, which is equally free from caustic; but for household purposes the ordinary soda crystals are likely to retain their hold, and are consumed in very large quantities as 'washing soda,' and under various fancy names.

Originally, of course, all soda crystals were made from Leblanc soda, and the great effort of the crystal makers was to find out how to obtain a good crystal from the vat or tank liquor direct. The bulk of the crystals made and probably all those of good quality were, however, produced from Leblanc ash by the same method as is adopted for their manufacture from the ammonia alkali which is now always used.

The ammonia alkali is dissolved in any suitable dissolver fitted with a mechanical agitator and fed with hot water. In a vessel 8 ft. diameter by 6 ft. high, 40 tons of 58 p.c. ash can be dissolved in 16 hours.

The solution is made to 1·3 sp.gr. hot, and is then pumped to settlers in which a small quantity of sodium sulphate is added, as commercial crystals require anything up to 1 p.c. sodium sulphate to give them the desired crystalline form. While settling the temperature of the liquor has to be maintained above 34°, the temperature of maximum solubility. If the settlers are large and sheltered there is usually little difficulty in this.

The liquor is run from the settlers into the crystallisers, which are iron vessels varying in different factories between the widest limits of shape and size. These vessels have in all cases a hole in the bottom stopped up with a long wooden plug. This hole is to permit the mother liquor from the crystallisers at the end of the crystallising operation to drain into shutes below, which convey it to collecting tanks or wells in the floor, from which it is pumped into the dissolver again to assist in making up the next batch. Across the top of the crystallisers from side to side is usually placed a number of bars or strips of metal, in order to support the crystals formed near the top of the liquor, and in this way to obtain fine large crystals.

The crystallisers are usually placed in double rows, with a mother liquor shute between them, in large, airy, lattice-sided sheds.

Crystallisers yielding 1 to 1½ tons of crystals usually finish in about one week in winter and a fortnight in summer.

After the mother liquor has been run off and the crystals allowed to drain well in the crystalliser, the crystals are taken out and placed in blocks on wooden shelves to drain for at least 24 hours, after which they are ready to pack.

Other crystals are crushed to comparatively small pieces in a crusher frequently of the Blake type and 'whizzed' in a centrifugal machine.

Soda crystals are either packed in wooden casks or kegs or in bags. When the casks or kegs are used it is usual to take the crystals from the draining shelf. When bags are used the better dried crystals from the centrifugal are taken, because the presence of any liquor in that case discolours the bag and the crystals.

The following is an analysis of a good brand of commercial soda crystals.:—

Na_2CO_3	36·60
$NaHCO_3$	0·25
Na_2SO_4	0·14
NaCl	0·15
Water (by diff.)	62·86
	100·00

The mother liquor eventually contains too much sodium chloride to be used again. It is therefore evaporated to dryness and the residue, which will contain about 29 p.c. Na_2O and 34 p.c. NaCl, is sold for what it will fetch. This necessity recurs at such long intervals that if the residue is thrown away the debit on the soda crystals made is negligible.

Commercial soda crystals are sometimes adulterated with Glauber's salts, specially manufactured in 'soda-fashion,' and it is said that now and then Glauber's salts are vended as 'best Scotch soda,' but it is hardly credible that such an easily discoverable fraud is frequently committed.

Mactear (Eng. Pat. 10651, 1884) has constructed an apparatus for obtaining soda crystals in a granular form, by subjecting the solution during crystallisation to the combined action of cooling by cold-water action from the outside, and mechanical agitation.

In another patent (Eng. Pat. 1989, 1886) he describes compressing those granular crystals into the shape of tablets, cakes, or blocks, most conveniently of a rectangular form, so that they can be packed without waste of space.

Crystal carbonate. This is the name given originally by Messrs. Gaskell, Deacon & Co. to a very pure monohydrated sodium carbonate, Na_2CO_3,H_2O, obtained by direct evaporation from tank liquors, thoroughly carbonated with addition of bauxite, and afterwards purified from ferrocyanide by superheating to 180° (Carey, Gaskell and Hürter, Eng. Pats. 1161, 1881; 2939, 1879; 5310, 1882). This substance was absolutely free from caustic, silica, and alumina, and was altogether far superior to ordinary soda crystals, not merely in strength, but also in purity.

As in the case of soda crystals, however, the Leblanc vat liquor has been replaced by ammonia alkali, and the crystal carbonate is now obtained in a still purer state from this source.

The following is an analysis of crystal carbonate, made from ammonia alkali:—

Na_2CO_3	82·0
NaOH	0·0
Na_2SO_4	trace
NaCl	0·25
Water	17·5
	99·75

Crystal carbonate dissolves in water much more easily than ordinary soda crystals, because, instead of lowering the temperature, it slightly raises it in the act of solution, and because its grainy texture offers a much larger surface to the water than soda crystals do.

One ton of crystal carbonate contains as much alkali as 48 cwt. of soda crystals, and occupies only 65 cubic feet against 150 cubic feet occupied by 48 cwt. of soda crystals

Bicarbonate of Soda. Bicarbonate of soda was formerly made by the action of carbonic acid usually obtained by decomposing $CaCO_3$ with hydrochloric acid, on soda crystals.

The soda commonly employed was in the state of ordinary crystals; those of yellow colour or otherwise inferior quality could be utilised quite well. They were exposed to the action of the gas in apparatus of various shapes, made of brickwork, wood, or preferably of iron, holding up to 60 tons of crystals. They were connected in such way that the gas passed from one chamber to another. Large doors served for charging and emptying. A false bottom, made of laths, was laid down inside, below which the gas entered and above which the crystals were put up in regular layers. The space below served for holding the abundant drainage of mother-liquor caused by the fact that nine of the ten molecules of water of crystallisation were set free: $Na_2CO_3,10H_2O+CO_2=2NaHCO_3+9H_2O$. This liquor dissolved the small quantity of foreign salts and other impurities contained in the crystal soda, and ran off through a U-tube fixed in the chamber bottom. The end of the process was indicated by the stoppage of this flow, which generally occurred in from 6 to 9 days.

On opening the chambers the bicarbonate was found apparently in the shape of the crystals originally charged, but in reality only as a loose powder. It was very damp, and had to be dried in stoves heated to a temperature not exceeding 45°. Dry and warm carbonic acid, if not too expensive, would have greatly expedited the drying, which generally lasted 8 or 10 days.

Mathieson and Hawliczek (Eng. Pat. 150, 1886) prepared pure sodium bicarbonate from black ash, crude sodium sulphide, or crude bicarbonate, as obtained in the ammonia-soda process, by dissolving those products in a solution of sodium chloride of from 16 to 19 p.c., and treating the solution with carbon dioxide, whereby nearly all the bicarbonate was precipitated in a crystalline form. The bicarbonate is said to be obtained nearly in a chemically pure state. With impure materials, as black ash or crude sodium sulphide, the CO_2 first precipitates iron, alumina, and silica, and these are separated by filtration before precipitating the bicarbonate itself.

A totally different process from that formerly employed is that of Carey, Gaskell and Hürter (1881 and 1882). It is principally based on the employment of the 'crystal carbonate' previously described, which is exposed in a revolving cylinder to the action of pure carbon dioxide, entering at one end and escaping out of the other; after being passed in a pipe upwards, say 30 ft., and down again, it is sufficiently deprived of moisture, and is re-introduced into the first cylinder, or else into another cylinder. A cylinder of 8 ft. length and 5 ft. 6 in. wide contains a charge of 1½ tons, and produces 2 tons of bicarbonate. It is supported on hollow trunnions; gas-pipes pass through these, and upwards inside the cylinder, so that they are not stopped up by the salt. By taking the exit pipe upwards for about 30 ft. and down again, and thus cooling the gas, a difference of temperature is produced which effects a sufficient circulation of the gas, while at the same time the excess of moisture is condensed, and the water is run off before the gas passes again into the cylinder. This circulation is in practice best promoted by mechanically pumping the gas back again. The temperature rises very much during the absorption, but the cooling action of the air keeps it down; practically, the bicarbonate made in this way—that is, under a certain pressure—is very strong, containing about 97 p.c. real $NaHCO_3$, against 87–90 p.c. in the old process. The moisture must be regulated; if the mass becomes too dry, the carbonic acid introduced must be moistened by means of a small coke tower. With the progress of absorption the temperature falls again, and it is finished in 5 or 6 hours.

The patent contains also provision for employing impure carbon dioxide, by passing the gas through a series of absorbing cylinders; but this process does not seem to be in practical use. Anhydrous monocarbonate can also be used (Eng. Pat. 2876, 1882) by introducing steam together with carbonic acid.

The bicarbonate made by this process had almost superseded that made by the old process, when it was itself displaced by the bicarbonate made in the ammonia-soda process. This formerly could not be immediately employed for use as baking powder, &c., owing to the ammonium compounds it contains. Mond and Jarmay (Eng. Pat. 2996, 1884) found that on dissolving the crude bicarbonate in warm water and cooling pure bicarbonate of soda crystallises out and the ammonia salts remain in solution.

They dissolve the crude salt at 65°, filter off the insoluble impurities and allow the solution to cool. The bicarbonate separates out in granular crystals, which are drained, dried and ground. The solution can be made at a higher temperature in an atmosphere of carbon dioxide under pressure, but it must be cooled down to 65° before removing the pressure. The mother liquors can be used many times over until they get too rich in ammonia.

Jarmay (Eng. Pat. 23890, 1893) describes improvements made in this process, and states the crude bicarbonate is dissolved in a closed vessel provided with an agitator in which the temperature is maintained by a closed steam coil between 85° to 90°.

The escaping vapours containing NH_3, some CO_2 and steam, are passed through a multitubular cooler, where they are surrounded by mother liquor from a former operation.

The solution in the dissolver containing bicarbonate and some sesquicarbonate is passed through a filter press and then pumped into an iron tower containing many compartments and water cooled. Here the temperature of the solution is reduced to 72°. Lime kiln gas is pumped into the bottom of the tower and causes constant agitation. The carbonated liquor and precipitated bicarbonate runs from the bottom of the tower on to a filter and the mother liquor flows back to the dissolver through the cooler mentioned above.

Jarmay (Eng. Pat. 3889, 1893) describes the drying of the moist bicarbonate obtained as above in a long covered trough through which the bicarbonate is carried on a conveyor and through which also air, preferably mixed with carbon dioxide and heated to 95°, is blown.

Brock and Hawlicek (Eng. Pat. 8314, 1896) treat the ammonia soda roasted ash or the crude bicarbonate, after removal of the ammonia and part of the carbon dioxide, with steam and carbon dioxide, either in rotation or simultaneously, in order to obtain a pure bicarbonate.

The composition of commercial refined bicarbonate is given as—

$NaHCO_3$	97·2
Na_2CO_3	1·9
Na_2SO_4	trace
NaCl	0·35
H_2O	0·82
Insol.	0

(See Lunge's Alkali, vol. iii. p. 211.)

Sodium bicarbonate is chiefly used for the following purposes: as a chief ingredient of baking powder; as the carrier in the washing blue used in laundries; as the source of carbonic acid in the manufacture of mineral waters, for which it has the advantage over $CaCO_3$—which was formerly used for the purpose—of yielding double the quantity of CO_2 gas per unit of sulphuric acid and of leaving a soluble salt in the generator, viz. Na_2SO_4 instead of $CaSO_4$.

Sodium sesquicarbonate

$Na_2CO_3,NaHCO_3,2H_2O$

is made by Watts and Richards (Eng. Pat. 13001, 1886) by preparing a solution containing the above proportions and allowing it to crystallise not below 35°, keeping it agitated all the time. Such a solution can be prepared by heating sodium bicarbonate so as to deprive it of about one-third of its carbonic acid and dissolving the residue, or by adding to a hot solution of 84 parts of sodium bicarbonate 106 parts of sodium carbonate. This salt, which crystallises in fine needles, does not effloresce or deliquesce, and is readily soluble in water. Its principal employment is for wool washing.

The composition of sesquicarbonate is given as—

Na_2CO_3	46·57
$NaHCO_3$	37·0
Water of crystallisation	16·24
NaCl	0·18
Insol.	0·02

(See Lunge's Alkali, vol. iii. 212.)

THE MANUFACTURE OF SODA BY ELECTROLYSIS.

Practically all soda manufactured by electrolysis is produced by the electrolysis of sodium chloride.

The electrolysis of sodium chloride is described, together with the chief types of apparatus in use, under the article CHLORINE, vol. ii. p. 21.

The types of cell in that article are classified under four heads:—

I. The cells in which the electrolyte consists of fused sodium chloride.

II. The cells in which the electrolyte is a NaCl solution and in which the cathode and anode are separated by a porous partition.

III. The cells in which the electrolyte is a NaCl solution, but in which a moving cathode of mercury is used to remove the sodium produced from the action of the chlorine.

IV. The cells in which the electrolyte is a NaCl solution and which depend on specific gravity to keep apart the alkali and the chlorine.

Class I. The cells of this class, described p. 22, vol. ii., are the Vautin and Acker cells, in both of which the sodium is obtained as a lead sodium alloy. The sodium was obtained by Acker in the form of caustic soda by treating the molten alloy with steam in the absence of air, as described in his Eng. Pat. 14269, 1898.

Class II. With the exception of the Hargreaves Bird cell, all cells of this class yield a solution of caustic soda mixed with varying but always large quantities of sodium chloride. These solutions are concentrated and finished in apparatus similar to that described under the manufacture of soda by the Leblanc process, p. 49. Instead of the comparatively small quantities of salts which are deposited during concentration of Leblanc soda, much larger quantities of NaCl are thrown down and have to be fished out. This large quantity of salt is, after draining, usually washed with fresh cathode liquor from the cell, redissolved, and returned to the process.

Constitution of the cathode liquors from the various cells mentioned has been given approximately as—

The Griesheim cell, 8 p.c. NaOH, 20 p.c. NaCl;

The Townsend cell, 150 grms. NaOH and 213 grms. NaCl per litre;

The Finley cell, 7 p.c. NaOH.

In the case of the Hargreaves Bird cell, the liquor from the cathode compartment is, as described vol. ii. p. 23, a solution of carbonate mixed with sodium chloride.

Hargreaves (Eng. Pat. 21178, 1897) describes a method of separating the sodium carbonate from the salt. The sodium carbonate is generally produced in the form of soda crystals (washing soda).

Kershaw (Electrician, 1898, 547) gives the following analyses of two samples of the soda liquor flowing from this cell:—

	Sp.gr.	Na_2CO_3	NaCl	Molecules NaCl on 100 mol. Na_2CO_3
(1)	1·125	10·9 p.c.	0·94	15·6
(2)	1·094	10·44 „	0·1	1·73

Class III. The soda solution obtained from the decomposition of the sodium amalgam produced by cells of this class is very pure and free from NaCl. Its concentration, therefore, is not complicated by the production of 'salts.'

The solutions obtained are usually of about 45°Tw. (Lepsius, Ber., 1909). There is, therefore, about 4 tons of water to be evaporated before the solid caustic soda is obtained. The apparatus used for the concentration is similar to that described under Leblanc caustic soda, p. 49.

Class IV. As in the case of the cells with the porous diaphragm, the soda solution yielded by such cells as the Glocken cell contains large quantities of undecomposed sodium chloride, which has to be separated during concentration, drained, washed, and returned to process.

The constitution of the solution obtained is given in Chem. Zeit. 1901, 1171, as alkali, 6–12 p.c.; sodium chloride, 16–30 p.c.

A modification of the Glocken cell has been patented by the Society of Chemical Industry of Bale, 25118, 1909, the main point of which is the continuous saturation of the brine by causing the fresh electrolyte to flow from an upper to a lower electrode in order to drive backwards the ions of the newly formed products. The mode of operation consists in causing the electrolyte which has been partially impoverished at the upper electrode to be enriched again between the two electrodes by solid salt fed in a special manner. The advantage consists in obtaining a higher strength caustic soda with a good current efficiency. The theoretical considerations involved are dealt with in the patent.

4. Manufacture of Soda by other Processes.

ENUMERATION OF PROCESSES PROPOSED FOR MANUFACTURING SODA.

A. From common salt without converting it into sodium sulphate.

Potash (potassium carbonate) was used in the infancy of the manufacture of soda by Bergman, Hahnemann, Losh, and others, at a time when the former alkali was less valuable than the latter, the reaction being

$$K_2CO_3+2NaCl=2KCl+Na_2CO_3.$$

Lime slightly decomposes common salt, as first noticed by Scheele. In 1782 Guyton de Morveau and Carny obtained a French patent for this process, which they actually worked for some time, of course with very little success.

Lead oxide. Scheele, in 1773, noticed that common salt is (partially) decomposed by lead oxide, caustic soda and lead oxychloride being formed:

$$2NaCl+2PbO+H_2O=2NaOH+PbO,PbCl_2.$$

This process was at first considered one of the most favourable for the manufacturing of soda, and was worked both in France and England, where many patents were taken for it. It was the process first employed by Losh at Walker-on-Tyne, at the same works where also one of the later patents belonging to this class, Bachet's, received a serious trial in 1870, but with hardly more success than formerly. The incompleteness of the reaction is the principal obstacle to this process. A new patent for it is Knab's (Eng. Pat. 3082, 1877). The Société Anonyme Lorraine Industrielle (D. R. P. 23791) separates the caustic from the lead oxide by alcohol.

Romiquières (Eng. Pat. 14977, 1888) dissolves finely-divided lead in caustic soda by means of a current of air. The solution of Na_2PbO_2 thus obtained is treated with NaCl, and thus two molecules of NaOH for each molecule previously employed are formed, $PbCl_2$ being precipitated.

Berl and Austerweil (Zeitsch. Elektrochem. 1907, 165) describe the reaction as reversible, and give two equations:

1. For 'normal concentration'—

$$5PbO+H_2O+2NaCl+ \rightleftarrows 4PbO,PbCl_2+2NaOH.$$

2. For higher concentrations—

$$2NaCl+4PbO+H_2O \rightleftarrows 3PbO,PbCl_2+2NaOH.$$

The conversion of NaCl to NaOH being—

18°C.	50 p.c.
48°C.	43 „
74°C.	37 „

Vournassos (Eng. Pat. 23689, 1908) decomposes NaCl in a fused state by means of PbO.

Magnesia has been patented by W. Weldon

(March 1, 1866) for the following reaction: $2NaCl+MgCO_3+CO_2+H_2O=2NaHCO_3+MgCl_2$. The inventor expected to obtain all the soda as bi-carbonate, and to decompose the $MgCl_2$ into MgO and HCl. It is hardly necessary to point out that both of these reactions are far too incomplete for practical use.

Sulphide of iron is used by Reynaud (Eng. Pat. 14483, 1890), who heats it with NaCl, with the production of chlorine, sodium sulphate, and ferric oxide. This residue is mixed with coal and heated, producing a ferro-sodium-sulphide, which is treated by Blythe and Kopp's process (*see* below).

Oxalic acid and oxalates of ammonium and magnesium have been employed by various inventors. Their action is based on the slight solubility of the monosodium oxalate. None of these agents seems ever to have been tried on a large scale.

Hydrofluoric acid was proposed by Weldon (in 1866), and

Hydrofluosilicic acid by many inventors, these acids forming very slightly soluble sodium salts. A factory, working on a patent by Karcher and Tessié du Motay, existed for some years up to 1870, near Saargemünd, and the process seems to have given better results than might have been anticipated; but the various reactions on which it is based are too incomplete for practical use.

Calcium fluoride is employed by Brochon (Fr. Pat. 208754).

Alumina decomposes sodium chloride, in the presence of steam, at a very high temperature; this was utilised by Tilghman in 1847, and it has been taken up more vigorously since the discovery of native alumina in the mineral bauxite. Sodium aluminate is formed, and is decomposed as in the manufacture of soda from cryolite (*see* below). But the temperature required for the above-mentioned decomposition is too high, and the vessels employed cannot be made to last. On this account the attempts of Gossage (1862), of Grüneberg and Vorster (1876), and of Lieber (1878) have had no practical results.

Peniakoff (Fr. Pat. 405611, 1908) concentrates the impure liquors containing sodium carbonate, which are obtained in making pure alumina from bauxite to about 1·3 sp.gr., and then treats them with carbon dioxide, which precipitates sodium bicarbonate.

Clay, common salt, and water are employed by Kayser, Williams, and Young (Eng. Pat. 11492, 1887).

Silica and steam were employed as early as 1809 for decomposing common salt by Gay-Lussac and Thénard. This reaction was afterwards tried on a practical scale by Blanc and Bazille (1840), Fritzsche (1858) and others, especially by Gossage (1862), who brought sodium chloride in the state of vapour, along with steam, into contact with intensely heated quartz. The sodium silicate formed runs down in a fluid state. It is either used as such, or converted by CaO into NaOH, or by CO_2 into Na_2CO_3. This process was worked for some time, but the decomposition was too incomplete, the HCl was too difficult to condense, and the apparatus could not resist the intense heat.

Chromium oxide and steam has been patented by Swindells (1851), and Kessler (1687), but the reaction is quite incomplete.

Boric acid and steam have been patented by Margueritte (1855); boric acid alone by Garroway (Eng. Pat. 17395, 1889).

Steam alone decomposes NaCl at a very high temperature, and this reaction has been the subject of many patents, but unfortunately the reaction $NaCl+H_2O=NaOH+HCl$ proceeds only a very little way, otherwise this would be undoubtedly the simplest way of decomposing NaCl.

Magnesium sulphate (kieserite) is heated with sodium chloride and silica or clay in a current of air to 500° or 700°C. Chlorine is given off; sodium sulphate and magnesia remain behind (Townsend, D. R. P. 10641).

SODA FROM SODIUM SULPHATE.

Without converting it into Sulphide.

Lime. In 1789 Delius proposed this agent, and many other chemists followed him; in 1865 Hunter added the action of pressure. But the change is extremely imperfect as proved by Hill (Chem. News, 27, 165), and experiments made by Lunge (Dingl. poly. J. 238, 69), and by Cross and Bevan (*ibid.* 213, 137), confirm this.

Caustic baryta easily and completely decomposes sodium sulphate, but it is much too dear for practical use, in spite of several patents having been taken out for this process.

Caustic strontia was proposed for a very ingenious cycle of reactions by Ungerer (*ibid.* 188, 140). But as this process is very complicated, and includes the intervention of ammonia, it is far simpler and cheaper to employ Dyar and Hemming's process. There is also an American patent for strontium compounds (454136) by G. H. Gray.

Another process is suggested by Eichstädt (Eng. Pat. 15136, 1891), which depends for recovery of the $Sr(OH)_2$ on the following reactions—

(*a*) $SrSO_4+Na_2SO_4+8C=SrS+Na_2S+8CO$.
(*b*) $SrS+Na_2S+2H_2O=Sr(OH)_2+2NaSH$.

Calcium bicarbonate was patented in France by Pongowski (1872). Lunge (Dingl. poly. J. 243, 157) found that this causes no formation of sodium carbonate whatever.

Strontium carbonate is nearly always mentioned at the same time as

Barium carbonate. This has been tried in the dry way, by Kastner (1826) and Anthon (1840); in the wet way by many inventors, beginning with Kölreuter, in 1828. The reaction: $Na_2SO_4+BaCO_3=Na_2CO_3+BaSO_4$ is, however, incomplete, whatever temperature may be employed, even with excess of $BaCO_3$. But the decomposition is quite complete when barium bicarbonate is employed, or much more simply and cheaply by passing a current of CO_2 into an agitated mixture of $BaCO_3$ and solution of Na_2SO_4, as patented by Lunge in 1866. This process would be practicable, if a cheap method of recovering the $BaCO_3$ from the $BaSO_4$ could be found. At present it cannot compete with the ammonia soda process. Bramley (Eng. Pat. 1050, 1866) regenerates the barium carbonate from the sulphate, formed from the carbonate, by reducing the sulphate to BaS, then dissolving this in HCl, and treating the solution of $BaCl_2$

with hydrated magnesia and carbonic acid (a very hopeless process !).

In 1892 Nauhardt took a French patent (223339) for manufacturing sodium carbonate by digesting sodium sulphate with $BaCO_3$, prepared by treating BaS with CO_2.

Ammonium carbonates have been several times proposed for decomposing Na_2SO_4, first by Bower (1840). After the analogous process with NaCl had attained such complete success, the above has been again proposed, principally in order to recover the chlorine, as well as the soda, by interposing the manufacture of sodium sulphate and hydrogen chloride.

Alumina decomposes Na_2SO_4 in the presence of steam. This reaction, first proposed by Tilghman in 1847, furnishes sodium aluminate, which is easily decomposed by CO_2, Na_2CO_3 being formed and alumina being regenerated. In lieu of pure alumina, the mineral bauxite, found at Baux in the South of France, and in several other places, also at Irish Hill and Straid, County Antrim, can be employed. Several German patents by Löwig Brothers (93 and 1650, 1877) describe this process, in which, however, the manufacture of hydrated alumina is the principal feature. A modification of the alumina process was proposed by Vogt and Figge (D. R. P. 31675), another by Behnke (D. R. P. 7256).

Ph. B. and S. P. Sadtler (U. S. Pat. 877376, 1908; and Eng. Pat. 273, 1908) decompose alkaline sulphates by heating with excess of bauxite. Peniakoff (D. R. P. 80063) ignites bauxite or aluminium sulphate with sodium sulphate in the presence of alkaline sulphides or pyrites to produce sodium aluminate and sulphur dioxide. Projahn (D. R. P. 112173; Eng. Pat. 6790, 1899) heats salt-cake by itself, or with aluminous substances with exclusion of air, and with metallic iron at a dark red heat, and then lixiviates.

Silica decomposes Na_2SO_4, especially in the presence of coal, sodium silicate being formed, which is, indeed, one of the ways in which this compound is manufactured. It has been proposed to employ this as a soda-manufacturing process, by subsequently converting the sodium silicate into carbonate or hydroxide.

Hydrofluoric acid is mentioned in Weldon's patents of March 1, 1866, which are quite impracticable.

Calcium bisulphite and sodium sulphate yield calcium sulphate and sodium bisulphite. By heating the latter SO_2 is given off; the residual Na_2SO_3 is converted by lime into NaOH and calcium sulphite (Gutzkow's U. S. Pat. 198293, 1877).

A mixture of carbon dioxide and monoxide is supposed to decompose sodium sulphate at a red heat into carbonate and sulphur dioxide (Kayser, Young and Williams, Eng. Pat. 7355, 1885). This process is entirely useless, according to the investigation of Watson Smith, and Hart (J. Soc. Chem. Ind. 1886, 643). It has been tried on a practical scale at the Hautmont works, in France, in an apparatus similar to that of Hargreaves and Robinson for the manufacture of sodium sulphate, as the reaction is a very slow one. The drawbacks found there were: that the mass crumbles to powder, which stops the passage of the gas; that it is very difficult to keep the temperature at the proper point; and that all the sulphur escapes in the shape of sulphur dioxide, too dilute for utilisation (Lunge, Pariser Ausstellungsbericht, 1889, 15).

Crude phenol from coal-tar was proposed by Staveley (Eng. Pat. 17657, 1887). He agitates it with milk of lime and treats the resulting solution of calcium phenate with sodium sulphate. Calcium sulphate is precipitated; the solution of sodium phenate is decomposed by CO_2 into sodium carbonate and free phenol, which is used over again. *Cp.* also Staveley's paper, J. Soc. Chem. Ind. 1888, 807. This process is ingenious, but no doubt impracticable, especially owing to the hardly avoidable loss of phenol.

Calcium hydrosulphide is employed by Haddock and Leith (*cf. infra*, sub. *Soda waste*); also by Simpson (Eng. Pat. 17765, 1890) in the following way: Saltcake, nitre-cake, or the like are converted by $Ca(SH)_2$ into $CaSO_4$ and NaHS; this is carried on in closed vessels under a pressure of 60–80 lbs. per square inch. The clear liquor is decomposed by CO_2, and the H_2S set free is passed into milk of lime, in order to re-form the original calcium hydrosulphide. The soda is precipitated as $NaHCO_3$. A special application of this process is made upon low-class phosphatic minerals, which are suspended in water and treated with H_2S, the $Ca(SH)_2$ in solution being employed as above, whilst the enriched phosphatic mineral remains behind.

Calcium phosphates are employed in another patent of Simpson's (Eng. Pat. 18835, 1890). They are made to react with sodium sulphate; the sodium phosphate thus formed is converted by lime into caustic soda and calcium phosphate.

Soda from Sulphate, after converting it into Sulphide.

By heating sodium sulphate with coal a mixture of sulphide and carbonate is obtained, and this process has been proposed from a very early period down to 1839, among others by Berzelius, Gay-Lussac, Graham, and Liebig. It is, however, quite impracticable for soda-making, except as an intermediary for other processes, in the first instance.

By adding calcium carbonate, which is Leblanc's process, and has already been described.

Barium carbonate has been proposed by Reinar (1858), in lieu of calcium carbonate, but there is no advantage in this, and the cost is much too great.

Carbonic acid. In 1819 Atwood obtained an English patent for the decomposition of Na_2S by CO_2.

Since that date many inventors have tried to develop processes for the manufacture of carbonate of soda by this reaction, among others: Gossage (1838), Hunt (1861), Theissig, Verstract and Oliver, Claus Gomeg, Weldon, Thompson (1887), Chance (1888), Parnell and Simpson (1888), Mathieson and Hawlicek (1886), Gossage and Williamson (1888).

Na_2S requires more than one equivalent of CO_2 for complete decomposition, in fact it is necessary to convert nearly all the soda into bicarbonate

$$Na_2S+2CO_2+2H_2O=2NaHCO_3+H_2S.$$

The bicarbonate of soda separating out in fine crystals. Most of the processes suggested differed only in the apparatus used to bring the carbon dioxide and sulphide into contact.

Hunt, however, suggested treating the solid sulphide with carbon dioxide and steam. Mathieson and Hawlicek suggested the use of a brine solution instead of water to dissolve the Na_2S in order to take advantage of the lower solubility of $NaHCO_3$ in brine than in water.

Gossage and Williamson for some years made determined efforts to succeed with this process, but as far as is known, the sulphide process is not in use to-day. The difficulties were: (1) The technical difficulty of making the sodium sulphide itself, owing to its rapid action in the fused state on silicious material; (2) the fall in price of carbonate of soda owing to the development and cheapening of the ammonia soda process.

Sodium bicarbonate decomposes Na_2S thus: $Na_2S+2NaHCO_3=2Na_2CO_3+H_2S$. This reaction has been several times patented as a soda-making process (first by Wilson in 1840), but it seems to have a chance of success only as a means of purifying the liquor of the Leblanc process from the Na_2S always contained therein, and even there the action is not instantaneous.

On the contrary, sodium sulphide cannot be completely decomposed by CO_2, until about 1·6 equivalents of CO_2 are present to 1 equivalent of soda.

Alumina mixed with sodium sulphide is treated in a current of hot air by Liermann (1878); sodium aluminate is formed, and the gaseous products which escape are passed into a vitriol chamber.

Metallic oxides—such as copper, zinc, lead, iron or manganese oxide—have been very frequently proposed for decomposing Na_2S into a metallic sulphide and caustic soda. These proposals have hitherto mostly failed, first, on account of the difficulty of preparing Na_2S on a manufacturing scale; second, because in practice much more than an equivalent of the metallic oxide is required for effecting a complete decomposition of Na_2S; third, because the recovery of the metallic oxide from the sulphide is too costly, always entailing a loss of some of the metal, and never effecting a thorough utilisation of the sulphur. Such processes have been found more useful for purifying Leblanc's liquors from Na_2S. Still, attempts are continually made in this way—*e.g.* by Lalande (D. R. P. 41991, 1887). Lalande's process (which employs zinc oxide) has been found to effect the desulphurisation very well when tried at the St. Gobain works, but the separation of the ZnS and the regeneration of ZnO were found to be too troublesome.

Another form of this type of process has been invented by Ellershausen (Eng. Pats. 1015, 9112, 16676, 1890). He first forms a 'ferrate of soda,' similar to Löwig's (p. 48), by heating sodium carbonate with ferric oxide; on filtering a solution of sodium sulphide through a layer of ferrate of soda, the sodium sulphide is entirely converted into sodium hydroxide, which can be easily manufactured into commercial caustic soda. The sulphur is retained in the form of an insoluble ferrosodium-sulphide, to which Ellershausen gives the formula $Fe_2Na_2S_4$, and which retains one-sixth of the total soda.

Iron or **iron oxides** decompose Na_2S also at a red heat. Malherbe in 1778 proposed iron which was oxidised by the fire gases. Blythe and Kopp, in 1855, patented the use of iron oxides. Their process was tried on a large scale, but given up as useless; and this result has been confirmed by very extensive experiments on a manufacturing scale made by Lunge in 1865. There is a double sulphide formed in this process, the formula of which is stated by Stromeyer (Annalen, 107, 233) to be $Fe_2Na_2S_3$; this must be decomposed by CO_2 in order to yield Na_2CO_3 and FeS; but much H_2S escapes, and the FeS is much too impure to be burned for SO_2, as had been intended by Blythe and Kopp. The mass, moreover, contains much sodium thiosulphate and re-formed sulphate, and the furnace bottoms are very strongly acted upon, whatever material may be used for them.

Manufacture of Soda from Sodium Nitrate.

A very large quantity of sodium nitrate is indirectly converted into carbonate, inasmuch as it is first worked for nitric acid, and the residual acid sulphate ('nitre-cake') is worked up along with common salt in the ordinary decomposing pans. A considerable number of proposals have been made for making soda purposely from sodium nitrate, always, of course, with the condition of fully utilising the nitric acid as well. For some time artificial potassium nitrate was made by decomposing native sodium nitrate by *potassium carbonate*, chiefly in the impure form of carbonised 'vinasse,' from the manufacture of beet-root sugar; but this process has long been superseded by the use of Stassfurt potassium chloride.

Silica or *alumina* expel nitric acid from $NaNO_3$; so does *calcium carbonate*; in all cases the reaction takes place at such high temperatures that the nitric acid is decomposed, and although its re-composition can be effected by an excess of air and water, this costs too much to compete with the ordinary manufacture of nitric acid. The vessels employed are also corroded to an enormous extent. The advantage of obtaining the sodium in the shape of silicate, aluminate, or even hydroxide cannot compensate for these drawbacks.

Ferric oxide is used by Bradburn (Eng. Pat. 6710, 1889) to convert sodium nitrate (being the residue of Dunlop's chlorine process) into hydroxide.

Manufacture of Soda from Felspar.

Soda felspar has been several times proposed for manufacturing soda—*e.g.* by Ward and Wynants (1857 and 1864), who heated it with fluorspar, chalk, and lime; but this process has been found far too costly even for potash, and is not likely ever to answer for soda.

Manufacture of Soda from Cryolite.

This mineral is found mainly in one locality—namely, the bay of Evigtok, in South Greenland, where it was discovered by whalers, and again by Giesecké (1806–1813). Since 1849 it has become of some importance, because Julius Thomsen, of Copenhagen, proved it to be easily decomposable by lime, and to yield very pure soda and alumina. It was first worked upon a large scale in 1854, and several factories were erected for this purpose in various parts of Europe, but since 1865 the Pennsylvania Salt Manufacturing Company at Natrona, near Pittsburg, has obtained the control of nearly all the available mineral, so that no soda is made from it elsewhere.

Cryolite is a double fluoride of aluminium and sodium, of the formula $Al_2F_6,6NaF$; in the pure state it contains 12·85 Al, 32·78 Na, 54·37 F, corresponding to 24·23 Al_2O_3 and 44·17 Na_2O, but as it comes into trade it usually contains about 15 p.c. of impurities (galena, pyrites, fluorspar, limespar). It is a snow-white mineral, easily fusible, and soluble in concentrated sulphuric acid, but insoluble in hydrochloric acid.

Thomsen's process for working it up (which is the only one carried out in practice) consists in igniting it with calcium carbonate, when CO_2 escapes and soluble sodium aluminate, with insoluble calcium fluoride, remain behind:

$$Al_2F_6 \cdot 6NaF+6CaCO_3=Al_2O_3,3Na_2O+6CaF_2+6CO_2.$$

Finely-ground cryolite (100 parts) is intimately mixed with 150 parts of ground chalk, and some of the impure CaF_2 obtained in the process itself is added to the mixture, which causes it to decompose more completely and greatly increases the yield of valuable products. The mass must be spread in a thin layer, and must be heated to a red heat, but short of being fluxed, which would cause an imperfect decomposition. This is done in furnaces specially constructed by Thomsen for this purpose, which finish each charge of 9½ cwt. in 2 hours (*cf.* Lunge's Sulphuric Acid and Alkali, iii. p. 220).

The furnace charge is put, while hot, into the lixiviating tanks, and is methodically washed. The residue from this operation is an impure calcium fluoride (containing 62 p.c. CaF_2, 12 p.c. $CaCO_3$, 5·6 p.c. CaO, &c.). It is used for making bottle glass, for enamelling stone ware, as a metallurgical flux, &c. The solution of sodium aluminate obtained, which tests from 48°–60° Tw., is decomposed in revolving cylinders, or in vessels provided with agitators, by the carbon dioxide from a lime kiln.

The final result of the decomposition is stated thus:

$$Al_2O_3,3Na_2O+3CO_2+3H_2O=Al_2(OH)_6+3Na_2CO_3;$$

but in reality a compound of 45 p.c. alumina, 20 p.c. sodium carbonate, and 35 p.c. water is precipitated in a granular state, and must be freed from soda by long washing with hot water. This is carried on until the aluminium hydroxide contains only 2 p.c. of soda. Most of it is converted into aluminium sulphate by dissolving it in dilute sulphuric acid at 90°C., and boiling down the solution in copper pans to the consistency of treacle; it is then poured into moulds and solidifies on cooling. The richest commercial article contains 20 p.c. Al_2O_3.

The solution produced in the precipitating vessels is boiled down to 66°Tw., and on cooling yields a crop of extremely pure soda crystals, containing hardly more than ½ p.c. of foreign salts. The mother-liquors are so pure that they can always be taken back again into the process.

THE COMMERCIAL SODA TEST.

The commercial soda test used for trade purposes for both caustic soda and soda ash does not agree with the real percentage of Na_2O in the product. This is well known to the trade and is universally accepted under the name of the Liverpool test.

The discrepancy between real soda and the commercial test originated in the early days of the manufacture, when the equivalent of Na_2O was considered to be 32 and of Na_2CO_3 54.

The percentage of Na_2O in Na_2CO_3 was therefore considered to be 59·26 p.c. Na_2O. With the modern equivalents of 31 : 53, the actual percentage of Na_2O in Na_2CO_3 is of course 58·49 p.c. Na_2O.

In the same way, a caustic soda with an actual test of 70 p.c. Na_2O would, by the commercial test, be said to contain 70·92 p.c. Na_2O. A. C.

Sodamide $NaNH_2$ was discovered by Gay Lussac and Thénard. It is produced when a solution of sodium in liquid ammonia is allowed to stand at the ordinary temperature:

$$2Na+2NH_3=2NaNH_2+H_2$$

The reaction is considerably accelerated by the presence of a catalyst, such as platinised asbestos.

The usual method of preparation, and the one employed technically, consists in passing a stream of dry ammonia gas over metallic sodium heated to 300°–400° in an iron retort, when it is obtained as a waxy mass which is white when perfectly pure, but usually possesses a brownish or greenish tint due to the presence of traces of other substances.

When heated, sodamide softens at 149° and melts at 155°, forming a bright green liquid. At a red heat it decomposes slowly into its elements, but it may be distilled under ordinary pressure at about 400° with only slight decomposition. On exposure to air it absorbs moisture and carbon dioxide and becomes converted into a mixture of sodium nitrite, carbonate and hydroxide. Sodamide is an exceedingly reactive substance; heated in a current of carbon dioxide it glows, and is converted into cyanamide:

$$2NaNH_2+CO_2=2NaOH+CN \cdot NH_2$$

with nitrous oxide it yields sodium azide:

$$NaNH_2+N_2O=N_3Na+H_2O$$

It is decomposed by water with explosive violence, producing ammonia and caustic soda, and acts as an extremely powerful dehydrating agent. On this account it has of late years been manufactured on the large scale for use in the artificial indigo industry to replace the caustic soda formerly employed to remove water in the conversion of phenylglycocoll into indigo blue (*vide* INDIGO, ARTIFICIAL).

It has also found application in many other organic syntheses, and in the preparation of pure hydrazine, which it yields when heated with hydrazine hydrate.

Sodamide is an intermediate product in the manufacture of sodium cyanide. In this process, ammonia is led into a fused mixture of sodium cyanide, metallic sodium and carbon, when the sodamide first produced reacts with the cyanide to form disodiumcyanamide:

$$NaNH_2+NaCN=CN \cdot NNa_2+H_2$$

At a somewhat higher temperature, this compound is decomposed by the carbon present, being converted quantitatively into sodium cyanide.

Sodium nitroprusside $Na_2[Fe(NO)(CN)_5],2H_2O$ was discovered by Playfair in 1850. In order to prepare it, powdered potassium ferrocyanide is treated with twice its weight of concentrated nitric acid, previously diluted with its own volume of water. The mixture turns brown, and carbon dioxide, cyanogen, nitrogen, and hydrocyanic acid are evolved. As soon as solution is complete the liquid is warmed on a water-bath until a few drops give a slate-coloured precipitate on the addition of ferrous sulphate. It is then allowed to cool, when crystals of potassium nitrate separate out. The solution separated from the crystals is neutralised with sodium carbonate, filtered, and evaporated, when ruby-red crystals of sodium nitroprusside are obtained, which must be recrystallised to free them from admixed nitrate.

Another method of preparation consists in mixing a concentrated aqueous solution of ferrous sulphate with a solution containing equal parts of potassium cyanide and sodium nitrite, and allowing the mixture to remain at the ordinary temperature for five hours. Ferric hydroxide is deposited, and nitrogen and nitric oxide evolved. The liquid is then heated to 25° for a short time, made slightly alkaline with caustic soda, filtered, and the sodium nitroprusside obtained by evaporation and crystallisation.

Sodium nitroprusside forms ruby-red rhombic crystals, which contain two molecules of water of crystallisation. It dissolves in 2½ parts of water at 15°, and in a smaller quantity of hot water. The solution decomposes on exposure to light with separation of Prussian blue and evolution of nitric oxide. A concentrated solution is used as a reagent for the detection of small amounts of sulphur existing in the form of alkaline sulphide, a deep violet colour being produced. The colour is sufficiently intense to be noticeable in a solution containing only 0·0000018 grms. of H_2S in the form of ammonium sulphide, and by employing a capillary tube when applying the test one-tenth of this amount can be detected. The solution to be tested must be as concentrated as possible, and an excess of caustic soda in the liquid should be avoided, as this tends to prevent the development of the colour. The most suitable alkali to employ is ammonia, an excess of which has no such retarding action (Reichard, Zeitsch. anal. Chem. 1904, 43, 222).

The nature of the coloured compound produced is at present a matter of uncertainty, but it is probably represented by the formula $Na_4[Fe(NO{\cdot}SNa)(CN)_5]$ as the action of thiourea on sodium nitroprusside yields a compound $Na_3[Fe(NO{\cdot}NH{\cdot}CS{\cdot}NH_2)(CN)_5]$ which is a carmine red powder, closely resembling the substance formed from nitroprussides and sulphides.

SOFT CEMENTS *v.* LUTES.

SOILS. (1) *Classification.* Various classifications of soils have been proposed, the most general may be described as 'Genetic,' in which the position of the soil is determined by its origin, and the factors of climate and vegetation which have given rise to it. Tulaikoff (J. Agric. Sci. 1908, 3, 80) distinguishes:

1. Laterite soils developed in humid tropical climates and marked by a large proportion of hydrated ferric oxide and alumina.
2. Wind blown loess soils.
3. Soils of the dry steppes, distinguished by their richness in soluble salts, often alkaline.
4. Black soils (Tchernozem), containing large quantities of neutral humus.
5. Gray forest soils containing less humus.
6. Peat and ashy soils (Podzol). In this group are included all the soils of Great Britain.
7. Tundra soils.

Under British conditions we may distinguish between sedentary soils which have arisen *in situ* through the weathering of the underlying rock, and drift soils (soils of transport or alluvial soils) which have reached their present position through the action of running water or ice. The mixed soils of steep slopes which have either been washed or rolled down from above and containing angular fragments of diverse origin are sometimes separated as colluvial soils.

The farmer is accustomed to classify soils according to the ease or otherwise with which they can be worked, as sand, loams, and clays, with suitable subdivisions, *e.g.* sandy loams. These terms possess, however, widely different meanings according to the amount of rainfall which prevails, and can only be given any scientific value by correlating them with the mechanical analysis of the soil.

(2) *Proximate composition of the soil: mechanical analysis.* The texture of the soil and the manner in which it will behave under cultivation are determined by the relative proportions of sand, clay, calcium carbonate, and humus or organic matter which it contains. By sand is meant the coarser particles generally consisting of silica. As it is convenient to take an arbitrary limit of size, sand may be defined as consisting of particles smaller than 1 and coarser than 0·04 mm. in diameter. Such material is distinguished by the small amount of water it will contain and by its lack of coherence when dry. Clay consists of the finest particles present in the soil and is distinguished by the large amount of water that it will retain, by its plasticity and impermeability to water when wet, and by its power of shrinking and cracking when dry and swelling again on wetting. When diffused through water, the clay particles can be flocculated or coagulated by small quantities of various soluble salts (Hall and Morison, J. Agric. Sci. 1907, 2, 244). The properties of clay have been attributed to the presence of a small proportion of colloidal material, but it is doubtful if any such distinction can be drawn. If we take 0·002 mm. as the superior limit of size for the clay particles they run down without any break to particles of ultra-microscopic size which remain indefinitely in suspension in a neutral liquid, forming what might be described as a 'colloidal solution.' While clay mainly consists of hydrated silicates of alumina (kaolinite) there are also present notable proportions of zeolites—double silicates of alumina with soda, potash, lime and magnesia, also ferric hydrates and an admixture of very finely divided silica. For the purposes of analysis, the clay particles are divided by their size and not by their chemical composition. It is generally convenient to distinguish the groups of particles intermediate between sand and clay as silts.

All fertile soils contain some proportion of calcium carbonate finely disseminated throughout the soil. The proportion may vary from 60 p.c. or more in purely calcareous soils down to an inappreciable amount. Soils in which calcium carbonate and clay predominate are usually distinguished as marls.

The organic matter of soils consists in the main of the débris of previous vegetation. It is a mixture of various complex substances, some of them containing nitrogen, and from it a few distinct compounds have been isolated (*see* Schreiner, U.S. Bureau of Soils, Bull. 53 and 74). In fertile soils the organic matter usually possesses a neutral reaction and largely consists of calcium salts of the so-called 'humic acid.' Humic acid does not possess any distinct composition and though it may in part be identical with the humic acid that can be prepared by the decomposition of sugar, it cannot be obtained from soil in a state free from nitrogen. Humic acid is soluble in ammonia and other alkalis and may be extracted from soil, peat, &c., by first treating the material with hydrochloric acid to decompose the calcium humate, washing, and then extracting with an alkali solution from which it may be precipitated by acid. Soils in which the organic matter predominates are always black in colour, retentive of water and possessed of a very friable texture when dry. These peaty or boggy soils may be either acid in reaction, *e.g.* peaty and moorland soils, or neutral like the soils of the Fens.

The separation of the soil into its proximate constituents is known as a mechanical analysis, and the process consists in grading the particles (*a*) according to the velocity of the stream of water by which they can be carried, or (*b*) according to the time in which they will remain suspended in a column of water of a given height. The two methods are identical in principle and may be made to give similar results, but in most laboratories it is convenient to adopt the beaker method of separation by suspension.

A. *Sampling.* In Great Britain, the layer down to a depth of 9 ins. is usually considered to represent the soil. Probably a depth of 20 cm. would have been more satisfactory, since it represents more nearly the layer which is usually stirred by the plough, but so many analyses have now been made on the 9 in. basis that it is desirable to retain the convention. In certain cases of very shallow soils the soil changes suddenly at a smaller depth than 9 ins. into something which can hardly be regarded as sub-soil, as for instance, into pure chalk rock. In these cases, the sampling must be stopped at the line of division, which should be recorded. To obtain a sample two methods are commonly employed. In the first, a steel box, 6 ins. in section, is driven into the ground to a depth of 9 ins. and its contents removed. In the second case, an auger of not more than 2 ins. in diameter is employed. It is always necessary to take a number of samples on the same piece of land and mix them before analysis, and the advantage of the auger method lies in the number of samples that can be quickly obtained without unduly increasing the bulk of material to be handled. The first sampling is usually followed by a second one, taking the second 9 ins. to represent the subsoil. Small samples for examination, and even for approximate analyses, may be rapidly obtained down to a considerable depth by means of an auger such as is used by shipwrights. For details of sampling, Hall's 'The Soil' (Murray, 1908), p. 47, may be consulted.

The samples, on reaching the laboratory, should be spread out on shallow trays to dry at a temperature not exceeding 40°. The process is much accelerated by occasionally stirring and by crumbling down the lumps of the stiffer soils with the fingers before they become quite dry. The dried soil is passed through a brass sieve with holes 3 mm. in diameter, the lumps being gently worked down in a mortar with a wooden pestle. The material passing through the sieve is approximately weighed and also the material remaining on the sieve, which is then thoroughly washed on the sieve under a stream of running water. After drying, the stones which remain on the sieve are weighed to obtain the proportion of stones in the total sample as brought from the field. The material which passes the 3 mm. sieve is regarded as the fine earth for analysis.

B. *Mechanical analysis.* Two portions of 10 grms. and one of 50 grms. of the fine earth are weighed out. One 10 grm. portion is dried for 24 hours at 100°, and then ignited in an open basin over an Argand at a dull red heat with occasional stirring to obtain (1) hygroscopic moisture, (2) loss on ignition. The second 10 grm. lot is placed in a basin and covered with 100 c.c. of N/5 hydrochloric acid to dissolve out the carbonates and break up the calcium humate. The soil is rubbed up into a fine paste with a rubber pestle made by fixing a small solid rubber bung on a stout glass rod. After standing for an hour the soil is thrown upon a tared filter and washed until all acid is removed. The filter and its contents are then dried, the loss representing the hygroscopic moisture plus soluble salts. The soil is now washed off the filter with water containing about 1 c.c. of ammonia in 500 c.c. water on to a small sieve made with No. 100 brass wire cloth, the portion passing through being collected in a beaker 7 or 8 c.c. in diameter with a mark on the side 8·5 c.c. from the bottom. The material on the sieve is dried and weighed to represent the coarse sand and fine gravel. As the proportion of this coarse material is likely to be affected by irregular sampling when determined on 10 grms. only, it is advisable to repeat these operations on the 50 grm. sample without, however, preserving the material passing through the sieve. The residue after drying and weighing is then divided into 'fine gravel' and 'coarse sand' by means of a sieve with round holes 1 mm. in diameter. The beaker containing the portion of the 10 grm. sample which passed through the wire cloth sieve is now well stirred up with the rubber pestle, filled to the 8·5 mark with ammoniacal water and put aside to stand for 24 hours. The turbid supernatant liquid is then rapidly poured off into a large jar, and the deposit at the bottom of the beaker is rubbed up with a rubber pestle and more ammoniacal water as before. The operations of filling up to the mark, standing for 24 hours, and pouring off the turbid liquid are gone through as before and repeated every day as long as any material remains in suspension for the 24 hour period. Generally, 7 to 10 decantations will be sufficient, after which the bulk of turbid liquid is evaporated down and finally brought into a tared basin, dried and weighed. This fraction consists of clay particles less than 0·002 mm. in diameter, together with a certain amount of humus. After drying it is ignited as before and reweighed to obtain the weight of the 'clay.' The sediment from which the clay has been removed is worked up as before in the beaker, which, however, is only filled to the depth of 7·5 cm. The contents are allowed to stand for 12½ minutes only, when the liquid is poured off into a large jar as before. The operations are repeated until all the sediment settles in 12½ minutes and the liquid above is left quite clear. The contents of the second jar are now evaporated to dryness and weighed as in operation 3, before and after ignition; this fraction is designated 'fine silt' and consists of particles between 0·010 and 0·002 mm. in diameter.

The sediment remaining in the beaker is worked up afresh just as in the previous operations, the mark being now placed 10 cm. from the bottom of the beaker, and the time of settlement fixed at one hundred seconds. The sediment is dried and weighed as 'fine sand' while the portion that is poured off is obtained by evaporation as in the previous operations and is designated as 'silt.' The soil has thus been divided into the following series—

	Diameter in millimetres		
	Max.	Min.	
1. Stones and gravel	—	3·0	Separated by sifting.
2. Fine gravel . .	3·0	1·0	
3. Coarse sand . .	1·0	0·2	
4. Fine sand . .	0·2	0·04	Separated by subsidence.
5. Silt . . .	0·04	0·01	
6. Fine silt . .	0·01	0·002	
7. Clay . . .	0·002	—	

The sizes of the particles in the above groups, which is determined by the depth of the liquid and the time of settlement, are purely conventional and are those in use by agreement in the United Kingdom. For discussion of the method *see* Hall, Chem. Soc. Trans. 1904, 85, 950.

Chemical Analysis.

As in a mechanical analysis, certain conventions as to the sampling, nature of the solvent, and time of its action have to be adopted. The conventions followed below are general in the United Kingdom. The air-dried fine earth passing the 3 mm. sieve is taken and a portion of about 100 grms. is ground in a mill or broken in a steel mortar until it all passes through a sieve with round holes 1 mm. in diameter. Hygroscopic moisture and loss on ignition are determined as before.

C. Nitrogen is determined in 10 to 20 grms. of the ground material by Kjeldahl's process; no correction need be made for the nitrate that is present.

D. The determination of calcium and other earthy carbonates is of great importance, especially when the amount is low. It is not sufficient to determine the calcium, which may be present in considerable amounts as silicate, humate, &c., even when the soil is acid from lack of calcium carbonate. The earthy carbonates are best determined from the carbon dioxide evolved on treatment with acid, being calculated as though they consisted entirely of calcium carbonate. The most exact method, when the quantity involved is small, consists in liberating the carbon dioxide by treatment with dilute acid at low pressure, absorbing the carbon dioxide by dilute caustic soda in a Reiset tower and estimating the carbon dioxide by double titration, first with phenolphthalein and then with methyl orange as indicators (*see* Amos, J. Agric. Sci. 1905, 1, 322).

E. For the determinations of soluble constituents, 20 grms. of the powdered soil are placed in a flask of Jena glass, covered with about 70 c.c. of strong hydrochloric acid, and boiled for a short time over a naked flame to bring the acid to constant strength containing about 20·2 p.c. of pure hydrogen chloride. The flask is loosely stoppered, placed on the water-bath, and the contents allowed to digest for 48 hours. The solution is then cooled, diluted, and filtered. The washed residue is dried and weighed as the material insoluble in acids.

The solution is made up to a litre and aliquot portions are taken for the various determinations. The analytical operations are carried out in the usual manner, but special care must be taken to free the solution from silica and organic matter.

For determination of the potash and phosphoric acid, 50 c.c. of the solution is taken and evaporated to dryness, about half a gram of calcium carbonate being added during evaporation if the soil is poor in calcium. The contents of the dish are then ignited over an Argand or a Bunsen burner at a black or very dull red heat, the material being constantly stirred with a small glass pestle made by flattening out the end of a glass rod. After cooling, a few c.c. of water is added and the mass is worked up with the pestle, 50–80 c.c. of water is then added and the contents of the dish are boiled for half an hour. The solution is filtered off, the residue washed and the solution taken for determination of the potash by precipitation with platinic chloride in the usual way. The residue is washed back on to the dish, 50 c.c. of water and 10 c.c. of strong sulphuric acid are added and the whole boiled for half an hour. The solution is filtered and used for the determination of phosphoric acid by precipitation with ammonium molybdate, the molybdic acid precipitate being either weighed or estimated by titration. In some cases, finely divided ferric oxide comes through the filter paper in making up the solution, in which case 5 c.c. of hydrochloric acid is added and the whole evaporated nearly to dryness. This will bring the iron into solution, when it will not interfere with the determination.

Calcium, magnesium, iron, manganese, and sulphuric acid may also be determined in the hydrochloric acid extract.

The determinations just described give what is commonly called the total plant food in the soil. It will be seen that the quantities revealed are usually very great, if we consider that the layer of soil down to the depth of 9 ins. over an acre weighs from 2½ to 3 million pounds. As a rule, hydrochloric acid will extract something in the order of 0·1 p.c. of phosphoric acid and from 0·3 to 0·5 p.c. of potash, proportions which would correspond to about 3000 pounds of phosphoric acid and 10,000 lbs. of potash per acre, whereas the average crop will remove not more than 50 lbs. of phosphoric acid and 200 lbs. per acre of potash. It is clear that the quantities thus determined throw very little light upon the need, or otherwise, for the application of particular fertilisers to the soil, since the soil is shown to contain far more than is sufficient for a maximum crop. Even the extraction with hydrochloric acid does not measure the total amount of plant food in the soil; if, for example, the soil is completely brought into solution by fusion with ammonium fluoride as much as 2 p.c. of potash may be found in clay soils, and this quantity is in a sense the only absolute measurement that can be made.

In order to obtain by analysis some practical guidance as to the requirements of the soil, attempts have been made to discriminate between the total amount of plant food in the soil and that which may be regarded as readily available to the plant, *i.e.* that which is soluble in such weak solvents as may be at work under natural conditions. In the soil *in situ* there is every reason to suppose that the solvent action is carried on by water containing carbon dioxide in solution, partly by the natural soil water, and partly by the more concentrated solution of carbon dioxide which forms in contact with the plant roots that are always excreting carbon dioxide. As the gases entangled in the soil always contain more carbon dioxide than ordinary air (up to 5 p.c. by volume), the soil water contains a corresponding amount of carbon dioxide, and so becomes a more effective solvent of phosphoric acid and potash. Attempts have been made to use water saturated with carbon dioxide as an analytical agent to determine the available mineral constituents in the soil; but although this is the solvent with the best *à priori* justification, its use has not been general and there are not sufficient data obtained by its means for comparison. For the present, therefore, it must remain as a research method hardly available for general analytical purposes. It is customary to employ a solution containing 1 p.c. of citric acid to determine the phosphoric acid and potash that may be regarded as available. Other available constituents which may be taken to measure the fertility of a given soil are the nitrates and the ammonium compounds and also the humus compounds soluble in dilute alkali—the soluble humus or *matière noire*—which represents that part of the organic matter in the soil likely to be readily oxidised.

F. *Nitrates.* The soil sample must be rapidly dried in the steam oven, since slow drying at temperatures a little above the normal would result in the formation of nitrates. After drying the soil is roughly powdered and passed through a 3 mm. sieve as before. 200 grms. of the sample are then packed on a Buchner funnel, 6 ins. in diameter, connected with a filter pump. The soil is washed with successive portions of hot water, and if care is taken to avoid plastering the wet soil it is possible to wash all the nitrates through in the first 100 c.c. or so of the water that reaches the filtering flask. The nitrates in the solution thus obtained are estimated by the standard methods. In the Rothamsted laboratory, it has been found most convenient to proceed by reducing them to ammonia by the zinc-copper couple, as devised by Thorpe (Chem. Soc. Trans. 1873, 26, 541). Strips of thin sheet zinc about 6 ins. long and 1½ ins. broad are cleaned by immersion in dilute caustic soda, followed by very dilute sulphuric acid, and are then dipped in a dilute solution of copper sulphate until they have obtained a heavy black deposit of copper. After washing finally in ammonia-free water they are placed in a bottle with the soil extract and a crystal of oxalic acid. The bottle is kept in a warm place or an incubator at 25° for 24 hours, then the ammonia is distilled off and determined by titration or by 'Nesslerising.'

G. For determinations of the ammonium salts, 100 grms. of the soil are placed in a distillation flask with 2 grms. of magnesia and 100 c.c. of water. The tube from the flask is connected to a 100 c.c. pipette which leads into a filter flask serving as a receiver and containing 50 c.c. of standard acid. The distilling flask is placed in a water-bath kept at 30° and the filter flask is connected with a pump to maintain a partial vacuum. Distillation at this temperature proceeds for 6 hours, after which the pipette is disconnected and the acid titrated (*see* Russell, J. Agric. Sci. 1910, 3, 233).

H. *Available phosphoric acid and potash.* 200 grms. of air-dried soil are placed in a Winchester quart bottle with 20 grms. of citric acid and 2 litres of water. By the original method (*see* Dyer, Chem. Soc. Trans. 1894, 65, 115), the contents of the bottles are shaken up from time to time for 7 days and then filtered; but it has been shown that identical results can be obtained in 24 hours if the bottle is placed in an end-over-end shaker and kept in continuous agitation. After filtering, two portions, each of 500 c.c., are taken for the determination of phosphoric acid and potash by the methods previously described, after evaporation and incineration to get rid of the citric acid and dissolved silica.

I. *Soluble humus.* 10 grms. of the air-dried soil are treated with dilute hydrochloric acid in order to decompose the humus as in the method for mechanical analysis. After filtering and washing away the acid the soil is washed into a flask with 500 c.c. of 4 p.c. solution of ammonia. Flask and soil are then shaken for 24 hours, allowed to stand for several hours, and filtered until 200 c.c. of filtrate are obtained. This, representing 4 grms. of the original soil, is then evaporated to dryness in a tared basin and weighed. The basin and its contents are ignited to determine the ash and inorganic matter also present, the weight of which must be deducted from the weight of soluble humus previously obtained. Determinations are sometimes made of the nitrogen contained in the soluble humus; 50 c.c. of the extract are placed in a Kjeldahl distillation flask and evaporated nearly to dryness with the addition of 2 grms. of magnesia, after which the residue is digested with sulphuric acid and the nitrogen estimated in the usual way.

J. *Physical determinations.* In addition to the mechanical analysis of soils, several other physical constants of soil have, from time to time, been determined: for example, the maximum and minimum water capacity, the capillarity, the apparent and real density, the hygroscopic moisture, the heat evolved on wetting (Benetzung-wärme), specific heat, &c. The methods by which these determinations are made may be found in standard works on soil, but at the present time little value can be attached to the results. In many cases, the results are conditioned by the state into which the soil has been brought by the process of sampling, and as no satisfactory method exists of testing the soil *in situ* or bringing it in an unchanged condition into the laboratory, determinations made upon the usual samples possess no value. Further, in nearly all cases it is difficult to attach any interpretation to the results, *i.e.* to correlate them with the behaviour of the soil in the field. To two determinations, however, some practical value may be attached, viz. the hygroscopic moisture and the water content when the soil is in its optimum working condition and possesses a crumb structure. Hygroscopic moisture is usually determined by exposing the dried soil in a shallow tray to an atmosphere saturated with moisture at the ordinary room temperature. The dish containing the soil is placed under a bell jar over water and the interior of the bell jar is lined with filter paper which dips into the water below. It will be found almost impossible to obtain consistent results by this method because of the deposition of dew upon the dish or the soil. A better method is to place the soil in a shallow layer in a flat boat contained in a wide tube. The tube is immersed in a water-bath, maintained at a constant temperature of 25° by a thermostat, and a slow current of air is drawn over the soil, the air current being previously bubbled through a potash bulb containing water immersed in the same bath, so as to become saturated with vapour at the temperature of the experiment. Consistent and comparable results can in this way be obtained, and the hygroscopic moisture thus determines serves as a measure of the absorbing surface possessed by the soil. The water content of the soil in its optimum working condition is a conception introduced by F. K. Cameron (J. Phys. Chem. 1910, 14, 320) and represents that condition in which the soil can be cultivated and made to break down into small particles without puddling. Several pounds of the soil in a dried condition are placed in a large basin and slowly wetted with a fine spray of distilled water; the soil is carefully worked about with the hands to equalise the wetting, and it will be found that a point is eventually reached when the soil is distinctly moist and yet can be broken down to a crumb without getting into a pasty condition. If the moisture is increased beyond this point, the soil becomes obviously wet and gets sticky and puddled when any attempt to work it is made. The experimenter must use his judgment as to when the right point has been reached, then a sample of the soil is taken and its water content determined. With a little practice it will be found that successive results can be obtained with the same soil that agree within 1 or 2 p.c. The mean of several determinations may be taken as the optimum water content.

For further particulars, the following books may be consulted: Hall, The Soil, London, 1908; Hilgard, Soils, New York, 1906; Wiley, Principles and Practice of Agricultural Analysis, vol. i.; Ramann, Bodenkunde, Berlin, 1911.

Bacteria of the Soil.

A recognition of the importance of the biological factors at work in the soil is comparatively recent, indeed it can hardly be said to date further back than 1877, when Schloesing and Müntz showed that the formation of nitrates from the organic nitrogen compounds in the soil is a process brought about by a living agency. It is now agreed that as regards all the compounds of carbon and nitrogen present in the soil, their transformation into compounds capable of serving as food for plants is brought about by micro-organisms of one class and another, and that the fertility of the soil is very largely determined by the relative activity of the different groups. It is possible to show by the ordinary methods of plate culture that the soil contains bacteria in numbers of the order of 0·5 to 50 million per gram of soil, and there are several important groups of bacteria which do not grow on the usual gelatine media and therefore do not get included in this account. In addition to the bacteria, the soil possesses a micro-flora of yeasts, moulds, and other fungi, while latterly certain higher organisms—protozoa and amœbae, nematodes and the like, have been shown to play an important part in determining the activity of the lower organisms and therefore the fertility of the soil. A large amount of work has been done in the way of isolating and describing particular organisms present in the soil, but for practical purposes it is less important to identify species than to ascertain the collective activity of groups of organisms which possess the same function. Many efforts have been made to measure the activity of these various groups so as to obtain a quantitative estimate of the factors which determine the preparation or destruction of plant foods, but it cannot be said as yet that the methods devised are satisfactory, or have received general acceptance as leading to results which can be correlated with the fertility of the soil when determined by the yield of test plots.

The soil organisms may be conveniently grouped under the following heads:—

(*a*) Humus-making organisms which transform carbohydrates and other plant residues into humus.

(*b*) Nitrogen-fixing organisms which are capable of taking up free gaseous nitrogen and bringing it into combination in the material of which their own cells are composed.

(*c*) Ammonia-making organisms which attack the proteins and other less complex compounds of nitrogen and break them down with formation of ammonia.

(*d*) Nitrifying organisms which oxidise ammonium compounds and give rise to nitrites and nitrates.

(*e*) Denitrifying organisms which reduce nitrates to nitrites and to free nitrogen gas. In this group are generally included a further set of organisms, probably distinct, which set free nitrogen gas from organic compounds of nitrogen.

In addition to these main groups there are other organisms which sometimes play an important part in the soil, for example, the reducing organisms which form sulphides, hydrogen sulphide, and free sulphur from sulphates, and the iron organisms which secrete hydrated ferric oxide from solutions containing ferrous carbonate.

1. The relative predominance of organisms of the bacteria or fungoid type seems to be

determined by the reaction of the soil. In neutral or very slightly alkaline soils, bacteria predominate, in acid soils, micro-fungi are chiefly active and many important groups of bacteria, such as those bringing about nitrogen fixation and nitrification, may be entirely absent.

For the determinations of the number of organisms present in the soil, and indeed for all determinations of bacterial action, special samples must be taken.

A thin brass tube about 1 in. in diameter, sharpened at the lower end like a cork borer, is forced into the soil to a depth of 6 ins., then placed in a sterilised glass tube plugged with cotton wool for removal to the laboratory.

Another method which is more convenient, as yielding samples from various depths, begins by the construction of a special boring tool which can be driven into the ground. The tool consists of two strips of steel, ⅛ in. in thickness, 8 ins. long and 2 ins. wide, each bent down the whole length of the strip so as to form two wings, 1 in. wide, at right angles to one another. The edges are then bevelled off until the two pieces of steel can be put together so as to form a box, 1 sq. in. in section and 8 ins. long, in which position the pieces are retained by steel rings which can be forced over the two ends. The lower end of the tool is sharpened and it is then driven into the soil to the required depth of 6 ins. After removal, the rings can be knocked off, whereupon the box falls apart showing a square core of soil, any portion of which can be taken. In the laboratory the soil, still in a moist condition, is carefully broken down with a spatula and is worked through a sieve with holes 3 mm. in diameter. Two portions of 25 grms. are weighed out, one is dried to determine the water content, the other is shaken up for about 5 minutes with 250 c.c. of sterile physiological salt solution, containing 0·5 p.c. sodium chloride and 0·2 p.c. of magnesium sulphate. From this turbid liquid, 1 c.c. is pipetted off and added to another flask containing 99 c.c. of similar sterile salt solution. After well shaking 1 c.c. from this dilution is again transferred to a further 99 c.c. of sterile salt solution, and after again shaking 1 c.c. of this last dilution is added to a test tube containing 10 c.c. of nutrient gelatine, and the plate poured in the usual way. The plates are incubated for 8 days at a temperature of 20°; each plate represents 0·0001 gram of soil in its moist state. The gelatin medium usually employed contains 1 p.c. of beef extract, 1 p.c. of peptone, and 0·5 p.c. of sodium chloride with 10 to 12 p.c. of gelatin. A gelatin medium has the advantage of showing the liquefying organisms, of which a separate count can be made; humus-making organisms can also be distinguished by the furry appearance of the colonies or even by the formation of a brown ring, but the gelatin has the disadvantage of inhibiting a number of organisms which do not develop in the presence of much organic nitrogen. In place of the gelatin, 1·5 p.c. agar may be used; but though the agar plates permit of the growth of other organisms, they do not distinguish between liquefying and non-liquefying organisms, and many motile organisms work about the surface and may obscure the results or give rise to secondary colonies. Another useful medium is soil-extract agar made up as follows: Equal quantities of water and soil are boiled for half an hour and filtered, the liquid being further filtered through a Chamberland filter to get a clear extract. To the extract, 1 p.c. peptone and 1 p.c. dextrose or 1 p.c. dextrose alone are added, and the jelly is made up with 1½ p.c. agar as usual. This medium, without peptone, will permit of the growth of the nitrogen-fixing organisms, though it will inhibit the putrefactive, ammonia-splitting, and other organisms dependent upon combined nitrogen.

Another method of determining the collective action of the bacteria of the soil has been devised by Russell (J. Agric. Sci. 1905, 1, 261). He determines directly the oxidising power of the soil and finds it correlated with its fertility. The apparatus consists of a bulb of about 100 c.c. capacity with two tubes sealed into its neck, one of which is a long narrow tube dipping into mercury and constituting a gauge, while the other expands into a small flask partly filled at the beginning of the experiment with a solution of potash. 10 grms. of air-dried soil are placed in the flask with 2 c.c. of water, the flask is then sealed up and placed in a water-bath maintained at a constant temperature of about 20°. The apparatus is left for several days, whereupon the oxygen contained in the enclosed air is slowly converted into carbon dioxide which is absorbed by the potash, resulting in the diminution of the pressure of the enclosed air. Finally, the rate of oxidation is determined by the reduction in pressure which has taken place. It is necessary to make comparative trials with soils whose behaviour in the field is known, and while no absolute value can be given to the results, they are valuable as measuring the gross rate of bacterial activity in the soil and as supplying valuable indications of its fertility.

2. *Humus making organisms.* The decay of organic matter in the soil seems to proceed in two distinct fashions; in the presence of air the organic matter is broken down by micro-organisms of all kinds with the eventual production of carbon dioxide, water and ash. On the other hand, if the decay takes place under conditions which exclude oxygen, the process is more limited; carbon dioxide, marsh gas, hydrogen and other compounds are produced and there is left behind a black material containing more carbon but less oxygen and hydrogen than the original vegetable matter. Both aerobic and the anaerobic decay gives rise to brown or black humus compounds, but it is not certain whether the same organisms take part in both processes or which predominate under ordinary soil conditions of partial exclusion of oxygen. The anaerobic processes have been studied in some detail, and Omelianski has isolated two organisms which are capable of attacking carbohydrates like cellulose. In one case, the products are carbon dioxide, hydrogen, various organic acids, and humus; and the other, which is perhaps the more general, carbon dioxide, methane, butyric and other organic acids, are produced. The process may be readily illustrated by filling a flask with a nutrient solution containing 0·1 p.c. KH_2PO_4, 0·1$(NH_4)_3PO_4$, 0·05$MgSO_4$, and a trace of NaCl,

and introducing strips of filter paper with a small quantity of soil, or better still of pond mud. The flask is closed with an exit tube dipping down into water. After some days' incubation at 34°–35°, the filter paper will begin to disintegrate, at the same time gas will be given off consisting of a mixture of carbon dioxide, nitrogen, methane, and sometimes hydrogen. Humus may be either acid (as in peat soils), or neutral when it is formed in the presence of calcium carbonate, as is usual in soils.

Nitrogen fixing organisms. The first demonstration that the soil contains bacteria capable of bringing gaseous nitrogen into combination was due to Hellriegel and Wilfarth in 1886, who showed that the small nodules which may be found upon the roots of clover, beans, and other leguminous plants contain colonies of bacteria living symbiotically with their host plant, deriving from it the carbon compounds which they need, and handing over nitrogen which they have 'fixed' from the atmosphere with which the plant roots are in contact. It was found that clover and other plants possessing such nodules upon their root do become richer in nitrogen and that in practice the soil is markedly enriched by their growth. Such gains in nitrogen only take place when the seedling plant can become infected either by growing in soil which normally contains the organism, or by addition to a sterile soil of either the extract from a nodule of some infected plant or a trace of normal soil. To the organism the name of *Pseudomonas radicicola* has been given, and further investigation has shown that while only one general species can be distinguished it has, to a certain extent, been specialised by association with particular plants. Thus better results are obtained when beans are inoculated with the organism derived from a nodule of a bean plant than with organisms from a lupin plant, and in some cases (lupins and lucerne) this specialisation has proceeded so far that the plant is only very slightly infected by the neutral form of the organism which exists in ordinary soil. In the soil, the organism appears to exist in minute rod-shaped organisms in rapid motion which infect the plant by passing through the cell walls of the root hairs. Inside the plant, the organism first of all develops into much larger rod-shaped organisms, which finally become, in the nodules, characteristically bent or Y-shaped organisms known as bacteroids. It is possible to cultivate *Pseudomonas radicicola* on the non-nitrogenous media described above, as, for example, soil-extract dextrose, agar-agar, but the fixation of nitrogen under these conditions is inconsiderable.

From time to time, soils are found, the commonest example being peats and heaths of an acid reaction, in which *Pseudomonas radicicola* is not present, and when these soils are brought into cultivation, leguminous plants do not at first develop nodules and fix nitrogen. In this case, it may be desirable to proceed to an inoculation of the soil which, however, must first be rendered a suitable medium for the development of the organisms by the removal of its acidity and the addition of lime and phosphates. One method of effecting the inoculation is to strew over the field about $\frac{1}{2}$ ton to the acre of soil taken from a cultivated field on which the leguminous plants have been growing normally. Another method is to prepare an active culture of organisms from a nodule of the crop it is desired to sow, and with this prepare a large bulk of sub-culture by introducing it into ordinary tap water in which $\frac{1}{10}$ p.c. of dextrose and $\frac{1}{100}$ p.c. potassium phosphate have been dissolved. Into the large bulk of crude culture thus obtained after standing two or three days, the seed, tied up in a thin muslin bag, is dipped and allowed to dry somewhat before sowing, when it will be found to carry with it sufficient organisms to ensure inoculation. As a rule, the leguminous crop still grows rather indifferently after its first inoculation, and only really flourishes when grown for a second or third time after the organism has established itself in the soil. Many attempts have been made to improve the growth of leguminous crops in ordinary soil by inoculating them before sowing, but, except in the special cases just mentioned, no success has attended the process. Amongst ordinary farm crops, the only call for inoculation appears to occur with lucerne when attempts are made to grow this plant on soils which have not hitherto carried it, since lucerne does not seem to be readily infected by the neutral form of organism, such as that left by the clover which may have been regularly grown on the same soil previously. Since the discovery of *Pseudomonas radicicola*, other organisms have been discovered living free in the soil which are capable of bringing nitrogen gas into combination. Winogradsky isolated from pond mud and other similar material under anaerobic conditions a widely diffused organism called *Clostridium pastorianum* which breaks down carbohydrates with the formation of humus, butyric acid, &c., accompanied by the fixation of a small amount of nitrogen—two to three mgm. for each gram of carbohydrate destroyed. The most important of the nitrogen fixing organisms, however, is one discovered by Beijerinck, named by him *Azotobacter chroococcum*, which as such or as one of its closely allied forms has been isolated from soils in nearly all parts of the world. Its presence can be readily determined by adding a small portion of soil to 50 c.c. of sterile culture fluid containing per litre 10 grms. of mannite or glucose, 0·2 grm. each of potassium phosphate, magnesium sulphate, and sodium chloride, and 0·1 grm. of calcium sulphate and a trace of ferrous sulphate. The solution is placed in a small Erlenmeyer flask, $\frac{1}{2}$ grm. of calcium carbonate added, the flask is plugged and its contents sterilised. After adding the soil the flask is placed in an incubator at 25° for a week, by which time a considerable fermentation will be found to have taken place accompanied by the evolution of carbon dioxide and the formation of a brown scum upon the surface of the liquid. *Azotobacter* is a powerful oxidising organism, converting the carbohydrate into carbon dioxide and water, together with small quantities of lactic and acetic acid, alcohol and sometimes butyric acid. At the same time about 9 to 10 mg. of nitrogen are fixed for each grm. of carbohydrate oxidised. *Azotobacter* is a large oval organism, 4 to 5 μ in length and 3 μ in width. It differs from most bacteria in containing glycogen, so that it stains a deep brown colour with a solution of iodine. *Azotobacter* is not found on acid soils, the presence of calcium carbonate is essential to its development; to it and kindred organisms must be attributed a large share of the formation and maintenance of the stock of nitrogen contained in soils. Particularly to this agency do we look to explain the formation of the deep black soils of the Russian Steppes, the American North-West, Argentina, &c. It is, however, essential that the organism shall receive a supply of carbohydrate, by the oxidation of which it obtains the energy required to bring gaseous nitrogen into combination. At Rothamsted, it has been shown that the soil of the wheat field, from which the whole crop with the exception of a small quantity of roots and stubble is removed, gains very little nitrogen by bacterial agency, although the *Azotobacter* is present in the soil. An adjoining piece of land, however, on which the débris of grass and other wild vegetation fall back to the soil and is not harvested, there have been accumulations of nitrogen at a rate approaching 100 lbs. per acre per annum over a period of 25 years, and this case is parallel to the formation of the virgin soils above mentioned.

3. *The ammonia-making organisms.* As a group the ammonia-making organisms have not received much study, although recently it has been shown that the fertility of the soil must be largely determined by their activity. The greater number of the organisms found in the soil—the organisms, for example, which grow upon gelatin plates including such well known putrefactive organisms as *Proteus vulgare, Bacillus mycoides, B. mesenterieus vulgatus, B. subtilis, Bact. fluorescens liquefaciens, B. coli,* &c., must belong to this group. Their general function is well known; they are capable of attacking proteins and resolving them successively into a lower form of combination, amino acids, &c., until at last the nitrogen reaches the state of ammonia. In addition the soil contains other organisms not capable of dealing with the proteins, but resolving the simpler nitrogen compounds into ammonia. Of these the best known are the urea splitting organisms, *Micrococcus ureae, Urobacillus pasteurii* and *Planosarcine ureae,* which hydrolise urea with formation of ammonium carbonate and water. These organisms which are exceedingly abundant in stables, cow stalls, &c., are also present in the soil. The dependence of the fertility of the soil upon the numbers of the ammonia-making organisms has been made evident by the work of Russell and Hutchinson (J. Agric. Sci. 1909, 3, 111) on the effects of partially sterilising soil by heat or by exposure to the vapour of antiseptics like chloroform, toluene, &c. These investigators found that a soil which had been heated to a temperature of 100° for 2 hours and then placed under normal conditions favourable to growth gave rise to a much increased crop, the yield being in many cases doubled, while the amount of nitrogen in the plant became three or four times as great as that on the untreated soil. This increased crop was found to follow to a large extent the rate of the formation of ammonia in the soil, the ammonia in this case being taken up as such by the plant, because the nitrifying organisms had been destroyed. It was also found that the soil was not completely sterilised by the processes; the spores of certain groups resist the heat and develop to an unprecedented extent when the soil was once more placed under conditions favourable for growth. For example, a normal soil is found to contain about 8 million bacteria per gram before being subjected to treatment, and this number remained comparatively constant under ordinary conditions of growth. After heating the number of organisms per gram was reduced to as few as 60, but they increased rapidly from day to day when the soil was moistened and placed in the incubator, until in a fortnight's time they amounted to 40 millions or over per gram. The increase in fertility proceeded *pari passu* with the increased rate of production of ammonia, which in its turn depended on the increase in the number of organisms.

It was evident from the experiments that the heating had removed a factor present in ordinary soil which inhibited the development of the bacteria beyond a certain point, and it was found that the untreated soil contained a number of large organisms—protozoa, amoebae, &c., which derive their sustenance from living bacteria. Under normal conditions an equilibrium exists between the numbers of these larger organisms and of the bacteria, and as the heating process kills off the larger organisms entirely while still leaving some of the bacteria, the latter can develop to a hitherto unprecedented extent in the absence of the factor which previously kept them in check. Exposure of the soil to the vapour of chloroform, toluene, &c., for 48 hours, followed by its complete evaporation, has the same effect in destroying the larger organisms while leaving a certain number of the bacteria or their spores ready to develop as soon as conditions favourable to growth are obtained. With these volatile antiseptics, however, destruction of the larger organisms is not so complete nor the gain of fertility so large. It has not yet been found possible to apply these processes of partial sterilisation to increasing the fertility of soils in the open, but considerable success has attended attempts to deal with greenhouse soils, which, owing to their conditions of richness in manure, high temperature and water content, afford a specially favourable medium to the development of the larger organisms.

4. *Nitrification.* The process of nitrification and the factors by which it has been governed have long been worked out in a practical way. For example, in the *Instruction sur la fabrication du nitre: Par les régisseurs Generaux des poudres et saltpetres,* 1777, the formation of nitre beds is carefully described. They were made up of earth containing a certain amount of calcareous matter, mixed with dung and other nitrogenous residues. They were protected from the weather and carefully watered from time to time with diluted urine and other materials containing nitrogen. After two or three years, the contents of the bed were lixiviated, and the solution of calcium nitrate obtained was concentrated and treated with potassium sulphate, whereupon potassium nitrate could be crystallised out of the clarified mother-liquors. It was thus recognised that

soil is capable of converting organic compounds of nitrogen into nitrates in the presence of a base like calcium carbonate, and that warmth and a certain proportion of moisture are factors favourable to the process.

That the process was due to a living agency was first demonstrated by Schloesing and Müntz in 1877. These investigators showed that the action ceased if the soil was heated to the temperature of boiling water or was kept in contact with vapour of chloroform and similar antiseptics, and further that it only took place between the temperatures of 5° and 55°.

Warington, who continued the investigation, further showed that there are two stages of the oxidation process, one being the formation of nitrite followed by its oxidation to nitrate. Cultures were obtained capable of effecting one only of these changes, but owing to the difficulties of growing the organisms on the ordinary gelatin medium, it was not until Winogradsky, in 1890, devised a medium of silica jelly containing no combined nitrogen that the organisms were finally isolated in a pure state. Winogradsky obtained from soils in all parts of the world a single organism which he called *Nitrobacter*, capable of transforming nitrites into nitrates, but he obtained two organisms, *Nitrosomanas europea* in the soils of the old world, and a second *Nitrococcus javanesis* from the soils of Java, America, and Australia, which will transform ammonia into nitrites. The conditions of the activity of these organisms appear to be the absence of excess of organic matter, a neutral or faintly alkaline medium with some base in reserve to combine with the nitric acid produced, and the absence of any excess of alkaline carbonates or chlorides. It has been found possible to accustom the organism by successive cultivations to a toleration of ammoniacal and organic solutions much stronger than would normally inhibit its development. The organism derives the carbon necessary to its growth from carbonates in the culture medium or carbon dioxide in the air with which it is supplied. The nitrifying organisms are confined, as indeed are all bacteria, to the surface layers of the soil, being rarely present in subsoils at greater depth than 2 ft. They may be entirely absent from the soils of heaths of peaty bogs which are acid in their reaction, but are abundant in waters of shallow wells and rivers. Their development is promoted by warmth, by stirring the soil, and by free aeration. It was formerly considered that as the higher plants obtain their combined nitrogen almost entirely in the form of nitrate, the fertility of the soil must be determined by the activity of the nitrification process going on in it, but it is now considered that the nitrification process is only the end term of the oxidation of organic compounds of nitrogen, and that it proceeds as rapidly as ammonia can be supplied by the ammonia-making organisms above described. It is found, for example, that ammonia never accumulates as such in normal soils, whereas nitrates do. Thus the activity of the ammonia-making organisms is the factor determining the rate of production of nitrates, and therefore the fertility of the soil.

5. *Denitrification.* It was observed by Warington that when a soil containing organic matter and sodium nitrate was water-logged so as to deprive it of air, there was a considerable development of nitrogen gas accompanied by a loss of nitrogen to the soil. Gayon and Dupetit isolated two organisms from sewage which would reduce nitrates to nitrogen gas in the presence of organic matter, the action being chiefly carried on when oxygen was absent, but coming to a standstill when plenty of air was supplied so that the organism had no need to attack the nitrates in order to obtain oxygen. This property of reducing nitrates in the absence of free oxygen has since been found to be common to a large number of organisms. To the process the name of denitrification has been given, and it explains the fact observed in many experiments, particularly in pots, that when large quantities of organic manure like dung are used in conjunction with sodium nitrate, smaller returns are obtained than when either of the fertilisers is employed singly. In ordinary field practice, however, losses of this kind are hardly to be feared, because the soil rarely becomes sufficiently rich in active organic matter, nor so sealed from the access of air, as to lead to any attack upon the nitrate. At Rothamsted, for example, it has been found with the mangold crop that of the nitrogen applied as sodium nitrate, 78 p.c. is recovered when no organic or other nitrogenous manure is applied, while 61 p.c. is recovered when the nitrate is added to a plot which also receives dung at the rate of 14 tons per acre per annum, the recovery being reckoned on the excess of crop over that produced by dung alone. The lower recovery, when nitrate is used in connection with dung, is no more than might be normally expected under the law of diminishing returns. In certain circumstances, however, as in rice growing on water-logged soils containing much organic matter, it is inadvisable to apply sodium nitrate because of the denitrification that takes place. The term 'denitrification' is also more loosely applied to the loss of gaseous nitrogen which takes place whenever soils are brought into very high condition by excess of organic manures. There exist in the soils various groups of bacteria destroying organic matter with evolution of nitrogen gas, and the activity of the organisms increases with the amount of organic matter with which the soil is supplied. Thus a very highly manured soil tends to reach a condition of equilibrium in which the supply of nitrogen is balanced, in part, by the output of crop, but also by the accelerated activity of the organisms setting free nitrogen gas. For example, on the wheat field at Rothamsted, to which dung is applied at the rate of 14 tons per acre per annum, it has been found that during the 50 years, 1844–93, of the 200 lbs. of nitrogen annually applied, only about 26 p.c. was recovered in the crop and 25 p.c. was accumulated in the soil. Thus nearly 50 p.c. was wasted, and though some of it would have been removed by drainage water as nitrates, the greater part has been dissipated as nitrogen gas formed by bacterial action in the very rich soil. The condition of water logging which leads to denitrification may also be accompanied by the reduction of sulphates and the formation of black ferrous sulphide in ordinary soils. For the bacteria of sulphate reduction and other

sulphur organisms, also for iron organisms, *v.* Lafar, *infra.*

The great extent of the literature existing on soil organisms precludes the setting out of references, but further details, together with a full bibliography, may be found in Lafar, Technische Mycologie, 2nd Auf., Jena, 1904. A. D. H.

SOJA BEAN OIL *v.* Soya Bean Oil.

SOLANINE *v.* Vegeto-alkaloids.

SOLDERS. Solders consist of fusible alloys, which are used for joining metals together and are of various kinds, depending on the nature of the metals to be joined. They are distinguished by specific names, as hard-, soft-, white-, spelter-, silver-, gold-, aluminium-, copper-, tin-, plumbers'-, pewterers'-, and button-solder, &c. For whatever purposes they may be intended they should always be rather more fusible than the metal or metals to be united; and, to give the maximum strength, they should have about the same hardness and malleability as these metals. Solders may be divided into two classes, *hard* and *soft solders.*

Hard solders are commonly called *spelter* (a name which is also in technical use for cast zinc). Hard soldering is usually termed *brazing,* since the solders most commonly employed are similar to brass in composition. Brazing is used where greater strength is required than can be given by soft solder, or when an article has to stand a temperature that would cause soft solder to melt. Hard solders contain such metals as copper, silver, &c., and require a red heat to fuse them. The heat necessary is derived from either a forge fire, a benzoline or paraffin brazing lamp, or a brazing hearth, which is an arrangement of gas blowpipes (*v.* J. Soc. Chem. Ind. 1902, 21, 259). A brazed joint is commonly considered to be stronger than the adjacent metal, and is generally cheaper, easier, simpler, and quicker to make than a welded joint.

Soft solders are composed of lead and tin in varying proportions; sometimes bismuth is added. The following table (Tomlinson) of melting-points of a series of lead-tin alloys shows that soft solders melt below 300°; numbers 4 to 8 represent common solders :—

Tin-lead Solders.

No.	Tin	Lead	Melting-point	No.	Tin	Lead	Melting point
1	1	25	292°	7	1½	1	168°
2	1	10	283°	8	2	1	171°
3	1	5	266°	9	3	1	180°
4	1	3	250°	10	4	1	185°
5	1	2	227°	11	5	1	192°
6	1	1	188°	12	6	1	194°

The addition of bismuth lowers the melting-point; by varying the proportions of the constituents such alloys may be made, within certain limits, to melt at any desired temperature, even below 100°, thus admitting of various applications for electrical and other purposes. Examples are shown in the following table :—

Bismuth Solders.

Parts of tin	Parts of lead	Parts of bismuth	Melting-point	Parts of tin	Parts of lead	Parts of bismuth	Melting point
3	5	3	94·4°	1	1	1	123·3°
1	1	2	96·1°	2	2	1	143·5°
1	2	2	112·8°	3	3	1	154·4°
2	1	2	113·3°	4	4	1	160·0°

Soft solders are usually weaker in tensile strength than the joined metals.

Although soft solders are sometimes employed in conjunction with a mouth blowpipe, they are usually applied by means of a suitably shaped copper bit, miscalled a soldering iron.

In preparing solders, care must be taken to avoid two faults, want of uniformity and loss of a constituent that is either volatile or readily oxidised. Thus where copper, silver, &c., are to be mixed with tin, zinc, &c., it is necessary to melt the least fusible metal first; the zinc or tin is finally added, and after stirring, the mass is quickly cast. Efficient stirring, preferably with a piece of green wood, is necessary to secure uniformity of composition. Soft solders should be melted under tallow; they are cast in sticks, or run out into strips. Hard solders should be melted under powdered charcoal or borax. They may be granulated, or cast into small ingots and reduced to powder by filing. Gold and silver solders are generally rolled out into thin sheets and cut into narrow strips or else drawn into thin wire.

In the practical application of solders it is necessary that the metal surfaces to be united should be heated to a temperature above that at which the solder melts, and that the surfaces should be bright and clean, both mechanically and chemically. They may be cleaned mechanically by scraping or filing, and chemically by washing with a suitable acid or alkali. Since most metals tarnish when heated, owing to surface oxidation, it is necessary to protect the metal surfaces from air during the period of heating, or the solder will not wet the metals and adhere to them. Hence the use of *fluxes* in soldering. The flux used in hard soldering is *borax.* For soldering small articles, it may be prepared for use by rubbing a lump with water on a clean slate to a creamy consistency, and is then applied to the surfaces with a brush. When heated, the water is first expelled; at a red heat the anhydrous borax melts, and, flowing over the surfaces, it not only prevents access of air but also dissolves any surface films of oxides, producing double metaborates which remain dissolved in the excess of borax. It has been proposed to carry out brazing in an atmosphere of hydrogen or carbon monoxide (J. Soc. Chem. Ind. 1911, 30, 695).

Soft solders melt at temperatures below the fusing point of borax and other fluxes are therefore necessary. *Zinc chloride* solution is commonly used with most sheet metals, brass, copper, gun-metal, and bright iron. *Hydrochloric acid* is used with zinc and galvanised ware; *ammonium chloride* with copper and iron; *resin* with soft alloys and tinware; *Venice turpentine* or *Gallipoli oil* with pewter or Britannia metal; *Russian tallow* with heavy lead and *palm-oil candle* with light lead work. Lactic acid 1 pint, glycerol 1 pint, water 8 pints makes a good flux, as also does a solution of phosphoric acid in alcohol.

Resin possesses an advantage over acid fluxes like hydrochloric acid or zinc chloride as it does not induce subsequent corrosion. All excess of an acid flux should be thoroughly washed away. When it is necessary to use soft solder for repairing jewellery, resin cannot be used as it spreads all over the surfaces and is difficult to remove; zinc chloride should be used. The common prejudice against using zinc chloride when soldering electrical joints is stated by Lippmann to be groundless (Zeitsch. angew. Chem. 1909, 22, 2042). For a comparison between several fluxes, *v.* Samter (*ibid.* 1909, 22, 729).

Soft solders can be obtained in the form of narrow bore-tubes, with the central portion filled up with resin or other material, so as to obviate the necessity for using a separate flux. They may also be obtained, mixed with flux, in the form of a paste, *e.g.* (1) granulated soft solder is mixed with beeswax and impregnated with zinc chloride (J. Soc. Chem. Ind. 1906, 25, 269); (2) powdered solder is mixed with borax, ammonium chloride or other flux that leaves no acid residue and incorporated with glycerol or other inert and not too volatile substance (*ibid.* 1905, 24, 32); (3) powdered tin or solder is mixed with zinc chloride and celluloid paste and applied with a brush (*ibid.* 1903, 22, 1052).

For practical details of the art of soldering and descriptions of the requisite apparatus, consult books on metal working, Rowell's Hard Soldering, and Hobart's Brazing and Soldering.

Hard solders. *Gold solders.* Articles the fineness of which vary from 14 to 22 carats, may be soldered with alloys of lower grade prepared by fusing 2 grs. of silver and 1 gr. of copper with 1 pennyweight of gold of the same fineness as the article. These alloys are used in *dental* work. By replacing the 3 grs. of silver and copper by an equal weight of spring brass (2 of Cu, 1 of Zn), solders of good colour are obtained, suitable for use with *ornaments* and *jewellery.*

Coin gold is usually soldered with an alloy of pure gold 3 parts, spring brass 1 part.

Gold of a fineness of 12 carats or less may be soldered with 10 or 12 carat gold to which one-twelfth its weight of zinc has been added. A gold solder should not contain less than one-third its weight of gold. Lower grades of gold are best soldered with silver solder.

A good solder for *general use* contains gold 18, silver 4, copper 5, zinc 2 parts; another can be readily prepared by fusing 1 pennyweight of 18 carat gold with 5 grs. of spring brass. Among other jewellers' gold solders, the following may be mentioned; (1) best solder, gold 12½, silver 4½, copper 3 parts; (2) medium solder, gold 10, silver 6, copper 4 parts; (3) common solder, gold 8½, silver 6½, copper 5 parts; *v.* Gee, The Goldsmith's Handbook.

Antimony, arsenic, tin and lead should not be used in solders for gold.

Silver solders. These are employed a good deal in the arts; owing to the careful, sparing way in which they are used, most work requires but little finishing after soldering. The use of silver solders is not therefore unreasonably expensive; the results are extremely satisfactory. Besides being employed by jewellers and silversmiths, silver solders are also used for joining brass, copper, and even iron and steel.

Hard solders for *jewellers* and for *general use* contain: (1) silver 18, copper 4, zinc 1 part; (2) silver 15, copper 4, zinc 1 part. A good solder may be prepared by melting coin silver and adding one-third its weight of spring brass. An easy melting solder is prepared by fusing 2 parts of fine silver and adding 1 of spring brass, or by employing silver 4, copper 1, zinc 1 part, while an alloy of silver 16, zinc 1 part forms a very hard, white solder. A very common solder contains silver 1, brass 1, arsenic 1 part.

Many other silver solders are in use. A selection is given in the accompanying table, with remarks upon their uses. *See* also Gee, The Silversmith's Handbook.

SILVER SOLDERS.

Remarks on use	Parts of silver	Parts of spring brass	Parts of copper	Parts of zinc
Jewellers', hardest .	4	—	1	—
,, hard . .	16	—	3·5	0·5
,, easy . .	14	—	4·5	1·5
,, common, hard	12·5	—	6	1·5
,, ,, easy	11·5	—	6·5	2
,, easy, for chains	10	5	—	1
For steel . . .	18–19	2–3	1	—
Brass, gun-metal, bronze	1	1	—	—
,, ,, ,,	1	—	8	8
German silver, gun-metal, bronze	3	—	2	4
,, ,, ,, ,,	5	6	—	2
Brass, small articles .	2	—	5	3
Jewellers', instrument makers', very tough and fluid . .	11	—	13	—

Coin silver, rolled out thin, is an excellent solder for iron, copper, and very difficultly fusible brass.

Brass, bronze or copper to which 4 to 10 p.c. of silver has been added, forms a solder for thin sheets of mild steel (Diegel, Chem. Zeit. 1909, 33, 427).

A very full discussion of hard solders for *brass* is given by Schwirkus (Dingl. poly. J. 293, 64, 89), who recommends copper-zinc-silver alloys containing 40–50 p.c. of copper and 4–12 p.c. silver. For general use and repairs, an alloy of copper 43, zinc 48, silver 9 parts is best; for first soldering, copper 48, zinc 48, silver 4 parts should be used.

Copper-zinc-tin solders. Ordinary brazing processes are carried out with *spelter solder,* a mixture of equal parts of copper and zinc. It may be used on *brass, copper, iron* or *steel.* For pale brass, the proportion of zinc in the solder is increased, while for ironwork that has to be hammered afterwards the proportion of copper should be increased. The composition of a number of brazing solders is given in the following table.

Remarks on use	Parts of copper	Parts of zinc	Parts of tin
Soft spelter for brass . .	1	1	—
,, ,, ,, . .	4	3	—
Hard ,, gunmetal, iron-work .	2	1	—
,, ,, copper . .	3	1	—
,, ,, ,, . .	7	3	2
Soft ,, ,, and brass	4	3	1
Hard ,, brass (white or button solder) . . .	6·5	1	7·5

Ferrofix brazing process. This process for brazing broken iron parts, especially *cast iron,* was invented by Pich; the brass that cements the two pieces together is made to alloy with the iron surfaces as deep as $\frac{1}{16}$ inch. The *flux* used is a mixture of equal parts of sodium carbonat and boric acid, with a little sodium chloride. The *brazing liquid* is prepared by boiling cuprous oxide with concentrated borax solution and allowing the mass to cool down to a sort of paste. The method of procedure is to set the casting to be brazed on firebrick, in perfect alignment; mix fluxing powder with the brazing liquid and apply to the surfaces with a brush; heat, and apply more flux until it runs through the joint. Then apply ordinary spelter with a little flux until it flows through thoroughly. Remove the source of heat and continue adding spelter to the joint until the heat of the casting is insufficient to melt it (U.S. pats. 688030, 647632).

The spelter must not melt below 650°; hence hard brass must be used. The cuprous oxide of the brazing liquid transfers its oxygen to the carbon contained in the surface layers of the iron, which become decarbonised, while finely divided copper remains diffused through the joint. The hard solder quickly alloys with the copper and the new alloy immediately combines with the red-hot decarbonised soldering surfaces of the cast iron.

Solders for platinum. Fine gold, laminated and cut into shreds, is employed for soldering platinum. Pure silver may be used also and the following alloys have been proposed: (1) platinum 12, gold 7, silver 1 part; (2) platinum 1, gold 2, silver 1 part. Platinum joints are usually welded.

Solder for small steel springs. 18 carat gold may be used for repairing small, freshly broken springs; the spring must then be hardened and tempered.

Solder for German silver. An alloy of German silver 5, zinc 4 parts may be used; *v.* also *Silver solders* (p. 89).

Solders for aluminium bronze. (1) Tin 900, copper 100, bismuth 2 to 3 parts; silver chloride is used for flux; (2) gold 89, silver 4·5, copper 6·5 parts; (3) gold 54·5, silver 27, copper 18·5 parts; (4) the zinc-aluminium alloys given for aluminium (*v. infra*).

Soft solders. These contain tin, lead, and sometimes bismuth; for their melting-points, *v.* p. 88. The following table gives the composition of a number of solders, with remarks on their use.

SOFT SOLDERS.

Remarks on use	Parts of tin	Parts of lead	Parts of bismuth	Parts of zinc
Ordinary soft, plumbers', tinmen's . . .	1	1	—	—
Plumbers', coarse .	1	3	—	—
,, fine, for lead, zinc, tin, electrotype plates . . .	1	2	—	—
Tinmen's, coarse .	3	2	—	—
,, fine . .	2	1	—	—
,, rough, jobbing work	4	3	—	—
,, blowpipe work	4	2	1	—
Solder for tinned iron .	1	7	—	—
,, ,, can tops	16	10	1	—
,, ,, iron in stone	—	2	—	1
Pewterers', usual .	1	1	2	—
,, soft . .	3	4	2	—
,, ,, . .	3	4	1	—
,, ,, . .	2	1	1	—
,, ,, . .	1	4	2	—
,, rough work	2	1	1	—

Soft solders should be kept carefully free from zinc (*v.* J. Soc. Chem. Ind. 1909, 28, 1139). According to Sperry (Eng. and Min. J. 1909, 87, 1140) the addition of *cadmium* to soft solder makes it stronger and more fusible; an alloy of tin 2, lead 1, cadmium 1 part melts at 144·5° and can be used on lead, pewter, Britannia metal, &c.

Chemical solder. Tinfoil, cut to the size of the joint to be made, is painted over with a solution of sal-ammoniac, then placed between the two portions to be soldered together, and heated upon hot iron, or over a spirit lamp, until the solder melts, the pieces being held together by the hand during the operation. On cooling, a firm joint is the result. This method is very useful for the soldering of small articles together without a soldering iron—*e.g.* pieces of brass or copper wire, the ends of which should first be filed flat.

Solder for aluminium. No really good solder for aluminium is known, although considerably over fifty alloys have been proposed. The difficulty, which was known to Deville, arises from two causes, (1) the ease with which a film of oxide forms on the surface and the difficulty of properly removing it, and (2) the highly electropositive nature of aluminium, which causes electrolytic action to be set up, particularly if the soldered joint be wetted, and inevitably leads to disintegration at the joint. Ordinary soft solder will not do, but either pure tin or zinc may be used as solder. The zinc joint is very brittle, however, and the tin joint disintegrates since it slowly absorbs oxygen from the air. Aluminium-zinc alloys containing respectively 8, 12, 15, and 20 p.c. of aluminium, may be used (Tissier Bros.), the flux consisting of copaiba balsam 3, Venice turpentine 1 part, and a few drops of lemon juice. For heavy work, aluminium 12, zinc 80, copper 8 parts may be used; for light work, aluminium 6, zinc 90, copper 4 parts (Dagger, J. Soc. Chem. Ind. 1891, 10, 436). Mourey's solder, for blowpipe work, contains tin 6, zinc 3, aluminium 2, copper 1, silver 1 part. Frishmuth recommends tin 95, bismuth 5 parts, or tin 97, bismuth 3 parts as good soft solders.

Richard's solder (J. Soc. Chem. Ind. 1896, 15, 200; *cf. ibid.* 1899, 18, 281) is largely used; it contains aluminium 1, zinc 11, tin 29, 10 p.c. phosphor-tin 1 part. No flux is required, the solder being self-fluxing owing to the phosphorus it contains. For numerous other solders *v.* J. Soc. Chem. Ind. from 1892 onwards. It appears preferable to weld or rivet aluminium joints, rather than to solder them.

Cold soldering. This process may be adopted when the article to be soldered cannot be heated. The *flux* consists of sodium amalgam (1 part of sodium to 50 or 60 of mercury). The *solder* is a copper amalgam prepared as follows: copper is precipitated from a solution of its sulphate by means of zinc, and the spongy metal is washed, drained and shaken with twice its weight of mercury and a little dilute sulphuric acid. The pasty amalgam is quickly formed into small pellets; in a few hours they set to intensely hard lumps. The process consists in heating a pellet until mercury oozes from its surface in small beads, wiping these off and rubbing the pellet into a soft paste in a mortar.

The surfaces to be united are amalgamated with the flux, the pasty, prepared pellet then applied and the surfaces pressed tightly together. A perfectly hard joint is obtained in about three hours.

Autogenous soldering. In this process, soldering takes place by the fusion of the two edges of metal themselves without the interposition of a metallic alloy as a go-between; the metal acts as its own solder. Joints thus made are less liable to rupture when submitted to varying temperatures, &c., than when the common soldering process is employed; moreover, corrosion of the joint owing to electrolytic action does not occur. The process is adopted for the manufacture of sulphuric acid chambers and concentration pans, and the soldering is effected by directing a jet of burning hydrogen or coal-gas upon the edges to be joined together. Brass may be similarly soldered. For copper, iron, steel, platinum, and aluminium, the oxy-hydrogen or oxy-acetylene flame is necessary. Care must be taken to allow no excess of oxygen in the flame; with platinum, however, excess of hydrogen must be avoided, as it is absorbed by the molten metal.

SOLENITE *v.* EXPLOSIVES.

SOLIDE JAUNE *v.* AZO-COLOURING MATTERS.

SOLUBILITY. The term 'solubility' denotes the extent to which different substances, in whatever state of aggregation, are miscible with each other. That constituent of the resulting solution which is present in large excess is commonly known as the 'solvent,' the other constituent being the 'solute.' This, however, is merely a convenient distinction, not an essential one, and in cases where it cannot be easily drawn, the term 'miscibility' may be used as synonymous with 'solubility.'

It is proposed to give in this article an outline (1) of the methods available for the determination of solubility or miscibility, (2) of the general results obtained and their significance. For this purpose it is convenient to arrange the material according to the state of aggregation of the substances involved.

Solubility of gases. Two gases are miscible with each other in all proportions, that is, no definite value can be assigned for the solubility of *one gas in another*. The question of the solubility of *gases in solids* has been discussed elsewhere; such cases of absorption present peculiar features, inasmuch as the absorbed gas is not uniformly distributed throughout the mass of the solid, but is concentrated in the superficial layers, *v.* COLLOIDS.

The solubility of *gases in liquids* is a subject to which much attention has been devoted. The extent to which a given gas will dissolve in a given liquid is a function of the temperature and pressure. At any given temperature, the weight of the gas dissolved by a definite volume of the liquid is directly proportional to the pressure. This law was first formulated by Henry (Phil. Trans. 1803, 93, 29, 274), and its general validity has been confirmed by subsequent investigators (for example, Bunsen, Annalen, 1855, 93, 1; Khanikof and Louguinine, Ann. Chim. Phys. 1867, 11, 412; Woukuloff, Compt. rend. 1889, 108, 674; 109, 61). Strict conformity to the law, however, is exhibited only by those gases which dissolve in the liquid to a comparatively small extent. If the gas is highly soluble—for instance, ammonia or hydrogen chloride in water,—then the weight dissolved is no longer proportional to the pressure. An important extension of Henry's law was made by Dalton (Mem. Lit. Phil. Soc. Manchester, 1805, 1, 273), who showed that when a mixture of two indifferent gases is absorbed by a liquid each dissolves proportionally to its partial pressure.

The extent to which a gas is absorbed by a liquid is expressed by the 'absorption coefficient,' or, simply, by the 'solubility.' The absorption coefficient is defined as that volume of the gas (reduced to normal temperature and pressure) which is absorbed by unit volume of the liquid under normal pressure. Thus, if experiment shows that at $t°$ C. and p mm. pressure v cub. cm. of the gas are absorbed by V cub. cm. of the liquid, then the absorption coefficient $\beta=\frac{v}{V(1+\alpha t)}$. The solubility λ of a gas in a liquid, on the other hand, is defined simply as the volume of the gas absorbed by unit volume of the liquid; so that $\lambda=\frac{v}{V}$. In the following table are recorded the absorption coefficients for various common gases in water at different temperatures:—

Temp.	Oxygen.	Hydrogen.	Nitrogen.	Carbon dioxide.
0°	0·0492	0·0215	0·0237	1·713
5°	0·0434	0·0204	0·0211	1·424
10°	0·0385	0·0195	0·0191	1·194
15°	0·0346	0·0188	0·0173	1·019
20°	0·0314	0·0182	0·0159	0·878
25°	0·0286	0·0175	0·0147	0·759

The actual determination of the solubility of a gas in a liquid may be carried out in various ways. The method most commonly employed is to bring together known volumes of the gas and the gas-free liquid, to agitate them until saturation has been attained, and then to determine the diminished volume of the gas. Many forms of apparatus, based on this principle, have been suggested from time to time (Bunsen, Annalen, 1855, 93, 1; Mackenzie, Ann. Physik, 1877, 1, 438; Müller, *ibid.* 1889, 37, 24; Timoféeff, Zeitsch. physikal. Chem. 1890, 6, 141; Winkler, Ber. 1891, 24, 89; Setchenow, Ann. Chim. Phys. 1892, 25, 226; Steiner, Ann. Physik, 1894, 52, 275; Gordon, Zeitsch. physikal. Chem. 1895, 18, 1; Roth, *ibid.* 1897, 24, 114; Estreicher, *ibid.* 1899, 31, 176; Braun, *ibid.* 1900, 33, 721; Just, *ibid.* 1901, 37, 342; Skirrow, *ibid.* 1902, 41, 139; Knopp, *ibid.* 1904, 48, 97; Geffcken, *ibid.* 1904, 49, 257; Christoff, *ibid.* 1906, 55, 622; Usher, Chem. Soc. Trans. 1910, 97, 66; Drucker and Moles, Zeitsch. physikal. Chem. 1910, 75, 405). An alternative method is to saturate the liquid and then measure the volume of gas which is expelled on exhausting and boiling out (Hüfner, Ann. Physik, 1877, 1, 632; Dittmar, 'Challenger' Report, Physics and Chemistry, 1, 161; Pettersson and Sondén, Ber. 1889, 22, 1439; Bohr and Bock, Ann. Physik, 1891, 44, 318). Instead of expelling and measuring the gas present in the saturated liquid, it may be determined chemically if a suitable method is available (Schönfeld, Annalen, 1855, 95, 1; Carius, *ibid.* 1856, 99, 129; Roscoe and Dittmar, Chem. Soc. Trans

1860, 12, 128; Sims, *ibid.* 1862, 14, 1; Watts, Annalen Suppl. 1865, 3, 227; Winkler, Ber. 1889, 22, 1764; Bohr, Ann. Physik, 1900, 1, 244; Fox, Zeitsch. physikal. Chem. 1902, 41, 458; Clowes and Biggs, J. Soc. Chem. Ind. 1904, 23, 358). In certain cases an aspiration method of finding the partial pressure of a gas in its solutions may be utilised in the determination of solubility coefficients (Gaus, Zeitsch. anorg. Chem. 1900, 25, 236; Abegg and Riesenfeld, Zeitsch. physikal. Chem. 1902, 40, 84; McLauchlan, *ibid.* 1903, 44, 600; Jones, Chem. Soc. Trans. 1911, 99, 392).

As a general rule, the solubility of a gas in a liquid diminishes as the temperature rises, and a connection has been traced between this diminution and the viscosity of the liquid. It appears that the diminution in the absorption coefficient for any temperature interval is approximately proportional to the corresponding diminution in the viscosity coefficient of the solvent (Winkler, Zeitsch. physikal. Chem. 1892, 9, 171; Thorpe and Rodger, Chem. Soc. Trans. 1894, 65, 782). Cases, however, are known in which the solubility of a gas increases as the temperature rises. Thus, the existence of a minimum solubility has been established for hydrogen in water (Bohr and Bock, Ann. Physik, 1891, 44, 318) and for the rare gases in water (Estreicher, Zeitsch. physikal. Chem. 1899, 31, 176; von Antropoff, Proc. Roy. Soc. A, 1910, 83, 474). Further, Just (Zeitsch. physikal. Chem. 1901, 37, 342) has found that the solubility of nitrogen, hydrogen, and carbon monoxide in a number of organic solvents is greater at 25° than at 20°.

The factors which determine the solubility of a gas in a pure liquid are not clearly understood, but it is at least highly probable that, *ceteris paribus*, the greater the compressibility of the solvent and the smaller the volume change associated with the absorption of the gas, the greater is the solubility (*see* Ritzel, Zeitsch. physikal. Chem. 1907, 60, 319). In this connection, it should be pointed out that the relative volume change in a liquid resulting from absorption of a gas is proportional to the concentration of the gas (Angström, Ann. Physik, 1882, 15, 297; 1888, 33, 223; Mackenzie and Nichols, *ibid.* 1878, 3, 134; Nichols and Wheeler, Phil. Mag. 1881, 11, 113; Ritzel, *l.c.*). Further, the study of the solubility of gases in mixed organic solvents has revealed the existence of points of maximum solubility, such points corresponding with the occurrence of minimum surface tension (Skirrow, Zeitsch. physikal. Chem. 1902, 41, 139; compare Christoff, *ibid.* 1906, 55, 622).

Much attention has been devoted to the influence of salts and other dissolved substances on the absorption of gases by water. Provided there is no chemical action between the gas and the other dissolved substance it is generally the case that the gas is less soluble in the solution than in pure water at the same temperature (*see*, for example, Steiner, Ann. Physik, 1894, 52, 275; Gordon, Zeitsch. physikal. Chem. 1895, 18, 1; Roth, *ibid.* 1897, 24, 114; Braun, *ibid.* 1900, 33, 721; Knopp, *ibid.* 1904, 48, 97; Geffcken, *ibid.* 1904, 49, 257; Usher, Chem. Soc. Trans. 1910, 97, 66). An important result deducible from these and other investigations is that when a number of salts are arranged according to their power of lowering the solubility of one gas in water, the order is very nearly the same as when they are arranged with reference to their influence on the solubility of another gas. It appears, therefore, that the diminished solvent power of a salt solution as compared with pure water is mainly determined, not by the specific nature of the dissolved gas, but by some factor involved in the relationship of the water and the salt. What this factor is, has not yet been determined with certainty. It has been suggested that the influence exerted by salts is a function of the internal pressure or the compressibility of the solution (Euler, Zeitsch. physikal. Chem. 1899, 31, 368; Geffcken, *ibid.* 1904, 49, 257; Ritzel, *ibid.* 1907, 60, 319). On the other hand, interaction between the molecules or ions of the dissolved substances has been assumed to account for the influence of salts in lowering solubility (Levin, Zeitsch. physikal. Chem. 1906, 55, 503; Rothmund, *ibid.* 1909, 69, 523). Again, it has been suggested that the lower solvent power of a salt solution as compared with water is connected with the hydration of the salt (Rothmund, Zeitsch. physikal. Chem. 1900, 33, 413; Baur, Ahrens' Sammlung, 1903, 8, 466; Lowry, Trans. Faraday Soc. 1905, 1, 197; Philip, Chem. Soc. Trans, 1907, 91, 711; Hudson, Zeitsch. Elektrochem. 1908, 14, 821).

Solubility of liquids in liquids. As regards their mutual solubility, a pair of liquids is commonly assigned to one of three classes. They may be miscible in all proportions, they may be only partially miscible, or they may be practically immiscible. Such a classification, however, has only a general value, for the difference between the second and third classes is merely one of degree, and the line of division between the first and second classes is displaced by altering the temperature.

In finding the solubility of one liquid in another when the solubility is very small, as, for instance, in the case of chloroform or carbon disulphide in water, two methods may be adopted. One consists in bringing together a large known volume of the first liquid with a small known volume of the second, shaking until saturation has been reached, and then finding the volume of the second liquid remaining undissolved (Schuncke, Zeitsch. physikal. Chem. 1894, 14, 331; Bödtker, *ibid.* 1897, 22, 511; Herz, Ber. 1898, 31, 2669; Rex, Zeitsch. physikal. Chem. 1906, 55, 355). Another method is to shake quantities of the two liquids together until they are mutually saturated, and then remove portions of each layer for analysis (Chancel and Parmentier, Compt. rend. 1884, 99, 892; 1885, 100, 773; Walker, Zeitsch. physikal. Chem. 1890, 5, 196; Klobbie, *ibid.* 1897, 24, 616; Euler, *ibid.* 1899, 31, 364; Osaka, Mem. Coll. Sci. Eng. Kyoto, 1909–1910, 2, 21). Determinations are naturally made at various temperatures.

In the case of liquids the mutual solubility of which is greater than in the afore-mentioned cases, the method commonly employed is a synthetic one. That is, weighed quantities of the two liquids are put in a tube, which is then sealed and suspended in a bath of water or other suitable liquid. The temperature of the bath is altered until the contents of the tube become uniform and determinations of this point are then repeatedly alternated with determinations of the temperature at which, as indicated by the appearance of turbidity, the uniform contents of the tube begin to separate into two layers (Guthrie, Phil. Mag. 1884, 18, 22, 495; Alexéeff, Ann. Physik, 1886, 28, 305; Rothmund, Zeitsch. physikal. Chem. 1898, 26, 433; Bingham, Amer. Chem. J. 1907, 37, 549; 38, 91; Flaschner and MacEwen, Chem. Soc. Trans. 1908, 93, 1000). Experience shows that these two points, the one observed with rising, the other with falling temperature, are generally very close together, and the mean of the observed temperatures may be taken as the point at which the liquid is saturated.

For each temperature there are generally found two saturated mixtures of different composition, corresponding to the two layers obtained when the pure liquids are shaken up together. As a rule, the mutual solubility of two liquids increases as the temperature rises, and the compositions of the conjugate layers approximate more and more to each other. In such a case (Fig. 1), the two solubility curves, *i.e.* the curve representing the solubility of B in A and that representing the solubility of A in B, join at a point above which the liquids are completely miscible. As suggested by Masson (Zeitsch. physikal. Chem. 1891, 7, 500), who emphasises the parallelism between the case just described and the gradual approximation in density of a liquid and its saturated vapour, the temperature above which two partially miscible liquids become miscible in all proportions is called the 'critical solution temperature.' The existence of this temperature limit has been recorded for such cases as phenol and water, aniline and water, benzoic acid and water, carbon disulphide and methyl alcohol, methylethylketone and water. In these and other instances, it is further found that the middle points of the horizontal chords cut off between the two branches of the solubility curve lie on a straight line—another analogy with the density-temperature curve for a pure liquid and its saturated vapour (*see* Rothmund, *l.c.*). It is noteworthy that bismuth + zinc and lead + zinc furnish examples of limited miscibility in the fused state: the solubility curve for each pair is of the foregoing type (Spring and Romanoff, Zeitsch. anorg. Chem. 1897, 13, 29).

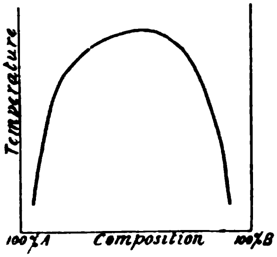


FIG. 1.

In a few cases—for instance, triethylamine and water, β-collidine and water, 1-methyl piperidine and water—the change of miscibility with temperature is the opposite of that described above. The mutual solubility increases as the temperature falls and there is a limit, known as the 'lower critical solution temperature,' below which the liquids are miscible in all proportions, and above which separation into two layers takes place increasingly as the temperature rises. The relation between solubility and temperature in such a case is represented in Fig. 2.

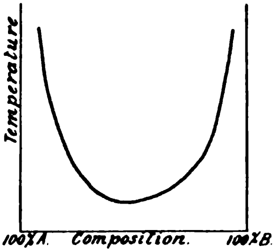


FIG. 2.

In two cases, nicotine and water (Hudson, Zeitsch. physikal. Chem. 1904, 47, 113), and 2-methyl piperidine and water (Flaschner and MacEwen, Chem. Soc. Trans. 1908, 93, 1000), both upper and lower critical solution temperatures are known, and the complete solubility curve is a closed ring. According to Rothmund (*l.c.*), this is the normal type of solubility curve for a pair of partially miscible liquids. There need not, however, be an upper critical solution temperature in every such case (Kuenen and Robson, Zeitsch. physikal. Chem. 1899, 28, 342), and the occurrence of a lower critical solution temperature has been held to be abnormal (Dolgolenko, *ibid.* 1908, 62, 499).

The mutual solubility of two liquids may be materially modified by the addition of a third substance. In this way two liquids which are miscible in all proportions may be made to undergo at least partial separation: for example, a homogeneous mixture of propyl alcohol and water, which are miscible in all proportions at ordinary temperatures, separates into two layers on the addition of salt. In the case of two liquids which are only partially miscible, the area of non-miscibility may be notably extended or reduced by the introduction of a third substance, and a measure of this influence is found in the effect of the third substance on the critical solution temperature. According to Timmermans (Zeitsch. physikal. Chem. 1907, 58, 129), who has made an exhaustive study of this phenomenon, the upper critical solution temperature is lowered when the solubilities of the third substance in the two liquids are of the same order of magnitude. If the third substance is much more soluble in the one liquid than in the other the critical solution temperature is raised, *i.e.* the area of non-miscibility is extended. It is noteworthy that when different salts are arranged according to their ability to cause the system water + propyl alcohol to separate into two phases, or according to their power to raise the critical solution temperature of water + phenol, the order is approximately the same as when they are arranged according to the magnitude of their influence on the solubility of gases in water. These effects have an obvious bearing on the well-known practice of 'salting out' organic compounds from their aqueous solutions.

Solubility of solids in liquids. The equilibrium between a solid and a liquid is established more slowly than that between two liquids, and this fact explains the precautions that must be taken if the solubility of a solid in a liquid is to be determined with rapidity and yet with accuracy. The solvent and the finely divided solid are put in a suitable glass vessel and shaken together at constant temperature, either intermittently by hand, or regularly by some mechanical arrangement. This is continued until the solution is saturated, when samples are extracted and analysed. The time necessary for the attainment of saturation varies from one case to another, and should be ascertained by preliminary experiments in which samples of the solution are taken out at intervals until the quantity of substance in solution is found constant. A guarantee that the value so found for the solubility is the correct one at the temperature of observation may be obtained by approaching the saturation point from the other side. A saturated solution is prepared at a higher temperature (on the supposition that the solubility increases with rising temperature), and is then put in a bath at the desired temperature, when the excess of solid in solution gradually separates out, the attainment of equilibrium being preferably facilitated by shaking or stirring. The analysis of the saturated solution obtained in this way ought to give the same result as the previous method (*see* Andreae, J. pr. Chem. 1884, 29, 456).

In the extraction of samples of the saturated solution an ordinary pipette may be used, with an auxiliary tube containing a plug of glass wool or cotton wool to keep back the solid. If the temperature at which the solution has been saturated is higher than the temperature of the room, the pipette may have to be warmed slightly to avoid crystallisation of the solid. It is, however, preferable in such cases to carry out the operation of filtration into a weighed vessel inside the constant temperature bath.

Many forms of apparatus for carrying out these various operations have been described (*see*, for instance, V. Meyer, Ber. 1875, 8, 998; Andreae, *l.c.*; Carnelley and Thomson, Chem. Soc. Trans. 1888, 53, 782; Meyerhoffer, Zeitsch. physikal. Chem. 1890, 5, 99; Reicher and van Deventer, *ibid.* 1890, 5, 560; Nicol, Phil. Mag. 1891, 31, 374; Noyes, Zeitsch. physikal. Chem. 1892, 9, 606; Arrhenius, *ibid.* 1893, 11, 392; Goldschmidt, *ibid.* 1895, 17, 152; Pawlewski, Ber. 1899, 32, 1040; Lumsden, Chem. Soc. Trans. 1902, 81, 350). For very high temperatures, such as the boiling point of the solvent and beyond it, the solubility apparatus must be specially modified (*see* V. Meyer, Ber. 1875, 8, 1000; Tilden and Shenstone, Phil. Trans. 1884, 175, 23; Goeckel, Chem. Zentr. 1897, ii. 401; Thiele and Calberla, Zeitsch. angew. Chem. 1906, 19, 1263; Schroeder, Zeitsch. anal. Chem. 1909, 48, 349; Tyrer, Chem. Soc. Trans. 1910, 97, 621). Attempts have been made to determine solubility by finding the temperature at which a minute quantity of the solid in contact with its solution neither increases nor diminishes in amount (Andreae, *l.c.*; Alexéeff, Ann. Physik, 1886, 28, 305; Schroeder, Zeitsch. physikal. Chem. 1893, 11, 453).

In the case of very sparingly soluble solids, such as the silver halides in water, the ordinary method of determining solubility is impracticable, because the amount of solid in the saturated solution cannot be estimated with any accuracy. For the silver halides in water, it is true, Whitby (Zeitsch. anorg. Chem. 1910, 67, 107) suggests heating the saturated solution with sucrose and sodium hydroxide under standard conditions and estimating colorimetrically the quantity of colloidal silver produced. But various physical methods are available for determining the solubility in water of sparingly soluble salts generally. Thus the electrical conductivity of the saturated solution may be compared with that of pure water, and the solubility of the salt deduced therefrom (Holleman, Zeitsch. physikal. Chem. 1893, 12, 125; Kohlrausch and others, *ibid.* 1893, 12, 234; 1904, 50, 355; Sitzungsber. K. Akad. Wiss. Berlin, 1901, 1018; Böttger, Zeitsch. physikal. Chem. 1903, 46, 521; 1906, 56, 83; Weigel, *ibid.* 1907, 58, 293). A knowledge also of the potential difference between a suitable electrode and the saturated solution of the sparingly soluble salt in question permits a calculation of the solubility (Goodwin, Zeitsch. physikal. Chem. 1894, 13, 641; Morgan, *ibid.* 1895, 17, 533; Thiel, Zeitsch. anorg. Chem. 1900, 24, 49; Immerwahr, Zeitsch. Elektrochem. 1901, 7, 477). Another method has been suggested by Biltz (Zeitsch. physikal. Chem. 1907, 58, 288), who shows that in the case of two salts giving a sparingly soluble compound by double decomposition, the ultramicroscope indicates when the solutions have been so far diluted that no precipitate forms. From such an observation the solubility of the precipitate may be calculated.

In the majority of cases, the solubility of a given solid in a given liquid increases as the temperature rises, and as a rule the solubility-temperature curve is convex to the temperature axis. No general law, however, is known which connects solubility and temperature. A decrease of solubility with rising temperature over the whole or part of the temperature range, has been observed in a number of cases, *e.g.* calcium sulphate, calcium hydroxide, sodium sulphate, ferrous sulphate (Tilden and Shenstone, Phil. Trans. 1884, 175, 23; Étard, Compt. rend. 1888, 106, 206, 740; Lieben and others, Monatsh. 1894, 15, 404; Lumsden, Chem. Soc. Trans. 1902, 81, 350). In some of these and other instances, points of maximum and minimum solubility occur on the solubility-temperature curve, *e.g.* for the calcium and barium salts of the fatty acids in water. Maxima are observed also in numerous cases where the dissolved solid forms a compound with the solvent: this occurs most commonly for the combination salt + water (*see*, for example, Roozeboom, Zeitsch. physikal. Chem. 1893, 10, 477). Discontinuities occur on the solubility-temperature curve at points where the solid in contact with the solution undergoes a change. Such breaks may be associated with the disappearance of one hydrate of a salt and the appearance of another (*see* de Coppet, Ann. Chim. Phys. 1883, 30, 429; Roozeboom, Zeitsch. physikal. Chem. 1890, 5, 198; 1893, 10, 477; Donnan and Burt, Chem.

Soc. Trans. 1903, 83, 335), or with the transition of one crystalline form of a substance into another (Rabe, Zeitsch. physikal. Chem. 1901, 38, 175; Müller and Kaufmann, *ibid.* 1903, 42, 497; Steele and Johnson, Chem. Soc. Trans. 1904, 85, 113).

Although there is no general law enabling us to predict the relation between solubility and temperature for a given solvent and solute, there is a close connection, deducible thermodynamically, between the heat of solution and the variation of solubility with temperature (Le Chatelier, Compt. rend. 1885, 100, 441; van 't Hoff, Kongl. Svenska Vet. Akad. Handl. 1886, 21, 17). According to this, the solubility of a solid in a liquid must increase with rising temperature when the process of dissolution is accompanied by the absorption of heat, and decrease with rising temperature when there is evolution of heat. The validity of this relationship has been confirmed by experiment (*see* Reicher and van Deventer, Zeitsch. physikal. Chem. 1890, 5, 559; van Deventer and van de Stadt, *ibid.* 1892, 9, 43; von Stackelberg, *ibid.* 1898, 26, 533).

As in the case of gases and liquids, the solubility of a solid in a liquid may be profoundly modified by the presence of a third substance. This may be due to definite chemical action; iodine, for instance, is more soluble in potassium iodide solutions than in pure water, and silver chloride, almost insoluble in pure water, dissolves readily in potassium cyanide solution. In other cases the solubility change appears to be connected with a displacement of equilibrium, as when the solubility of a salt is diminished by adding another electrolyte with a common radicle, or when it is increased by adding another electrolyte with both radicles different. The influence of salts on the solubility of non-electrolytes is more difficult to explain, the general, although not the universal, rule being that a non-electrolyte is less soluble in a salt solution than in pure water at the same temperature. The solubility of a non-electrolyte in water is sometimes raised, sometimes lowered, by the addition of another non-electrolyte. (For a detailed discussion of this whole question, *see* Rothmund's Löslichkeit und Löslichkeitsbeeinflussung, vol. vii. of Bredig's Handbuch der angewandten Physikalische Chemie; also Eyre, Brit. Assoc. Reports, 1910, 425.)

As regards the factors which determine the solubility of a given solid in a given solvent, little is known. From the mass of data available a number of regularities have been deduced, but these are of limited scope. Thus, for instance, it is known that, with water as solvent, the solubility of the monohydric alcohols diminishes as the preponderance of the alkyl radicle increases and that an increase in the number of hydroxyl groups introduced into a molecule leads to an increased solubility. For isomeric substances, certain rules have been deduced, such as that the more fusible isomer is also the more soluble in a given solvent, and that the ratio of the solubilities of two isomers in different solvents is approximately the same. *See* Lumsden, Chem. Soc. Trans. 1902, 81, 363; Rothmund, *l.c.* and Eyre, *l.c.*) J. C. P.

SOLUTION. The history of chemistry has been marked by constant speculation on the nature of the system formed when a substance dissolves in a liquid. The theories held at one time or another in regard both to the process of dissolution and to the constitution of solutions may be roughly classed as chemical or physical, according to the nature of the forces supposed to be at work. In either case, however, the experimental basis is furnished by the physical properties of solutions, and the utility and fitness of any theory of solution must be judged by the extent to which it is capable of interpreting these properties.

It is impossible within the limits of this article to deal exhaustively with the physical properties of solutions, but it is proposed to discuss the experimental results which have been achieved in connection with some of the more salient characteristics, and then to sketch the modern theories, based on these properties, which bear on the question of the nature of solution.

Density. It has been found that when aqueous solutions of different salts of the same molecular concentration (for example, 1 mol. salt to 100 mols. water) are compared, the density of the solution increases with the molecular weight of the dissolved salt. This rule, however, is not strictly valid unless the metals in the salts belong to the same group (*see* Kremers, Pogg. Ann. 1854, 92, 497; 1855, 94, 87, 255; Mendeléeff, Ber. 1884, 17 (Ref.), 155; Gerlach, Zeitsch. anal. Chem. 1888, 27, 271; 1889, 28, 290, 466; Charpy, Compt. rend. 1892, 114, 539). More definitely quantitative in character is the observation made by Valson, that if solutions of two salts AB and AB′ are compared, each solution containing 1 gram-equivalent in 1 litre of water, the difference in density is practically the same whatever the acid radicle A may be. Similarly the difference in density of comparable solutions of two salts AB and A′B with a common positive radicle is independent of B. There may therefore be assigned to each radicle, positive or negative, a certain figure or 'modulus,' such that the density of a normal solution of any salt can be calculated approximately by simply adding together the two values for the radicles contained in the salt (Valson, Compt. rend. 1871, 73, 441). This additive character of the density of dilute aqueous salt solutions has been confirmed by subsequent observers (*see* Ostwald, J. pr. Chem. 1878, 18, 353; Nicol, Phil. Mag. 1883, 16, 121; 1884, 17, 150; Bender, Ann. Physik, 1883, 20, 560). Bender was able to extend Valson's law of moduli on the strength of the observation that if Δ represents the difference between the densities of two salt solutions, each containing m equivalents of salt per litre of solution, then Δ/m is a constant for the two salts at a given temperature.

Investigation has shown that the density of a salt solution increases less rapidly than the concentration and that accordingly the value of the expression $\frac{s-1}{m}$, where s is the specific gravity and m is the concentration in gram-equivalents per litre, decreases as the concentration of the solution increases. If $\frac{s-1}{m}$ is plotted against m, the decrease is often found to be exceptionally marked in very dilute solutions, although the curves obtained by plotting $\frac{s-1}{m}$ against $m^{\frac{1}{3}}$ are practically straight lines (Kohlrausch and Hallwachs, Ann. Physik, 1893, 50, 118). More recently it has been found that within certain concentration limits the quantity $\frac{s-1}{m}$ is a linear function of the degree of dissociation as defined by Arrhenius (*see* Magie, Physical Review, 1907, 25, 171; Heydweiller, Ann. Physik, 1909, 30, 873; 1910, 31, 1063).

Much attention has been devoted to the character of the density-concentration curve in the case of aqueous solutions of sulphuric acid and ethyl alcohol. When the first or second differential of the sp.gr.—$\frac{ds}{dp}$ or $\frac{d^2s}{dp^2}$—is plotted against the percentage composition p, a series of straight lines is obtained in place of the continuous curve which results when s is plotted against p. It is maintained by some investigators that the discontinuities thus exhibited correspond with the formation of definite compounds between water and the dissolved substance (*see* Mendeléeff, Ber. 1886, 19, 379; Zeitsch. physikal. Chem. 1887, 1, 273; Chem. Soc. Trans. 1887, 51, 778; Pickering, *ibid.* 1890, 57, 64; compare Crompton, *ibid.* 1888, 53, 116; Arrhenius, Phil. Mag. 1889, 28, 30; Pickering and others, Chem. Soc. Proc. 1891, 105).

Closely related to the subject of density is the question how far the process of dissolution is accompanied by change of volume. A study of mixtures of organic liquids from this point of view has shown that the differences between the densities directly determined and the values calculated on the assumption that no change of volume occurs on mixing are considerably greater where associated liquids are involved than where both liquids are 'normal.' In the majority of cases where the mixed liquids belong to the latter class the observed density is less than the calculated value (Linebarger, Amer. Chem. J. 1896, 18, 429).

The investigation of solutions of such substances as paraffin, naphthalene, anthracene, dinitrobenzene and benzil in non-associated organic solvents has shown that the volume occupied by the solute in solution is approximately a constant, independent of the concentration and, with certain limitations, of the solvent. This volume, further, is approximately equal to the volume which the pure solute would occupy in the liquid state at the same temperature (Beilby, Chem. Soc. Trans. 1883, 43, 138; Nicol, *ibid.* 1896, 69, 142; Forch, Ann. Physik, 1905, 17, 1012; Lumsden, Chem. Soc. Trans. 1907, 91, 24; Dawson, *ibid.* 1910, 97, 1041, 1896; Tyrer, *ibid.* 2620).

The changes of volume which accompany the dissolution of a substance in water are much more notable. For some anhydrous salts and other substances, such as sodium hydroxide in dilute solution, the volume of the solution is actually less than the volume occupied by the pure solvent (*see* Macgregor, Chem. News, 1887, 55, 3). Attempts to find the volume occupied by a solute in aqueous solution are generally based on the assumption that the volume of the solvent in the solution is the same as if it were in the pure state. On this basis the molecular solution volume v_m, that is, the volume occupied by 1 gram-molecule of the dissolved substance, is given by the formula $v_m = \frac{m+w}{d} - \frac{w}{\delta}$, where m is the molecular weight of the solute in grams, w is the weight of water in which the gram-molecule is dissolved, d and δ are the densities of solution and pure water respectively (*see* Nicol, Phil. Mag. 1883, 16, 121; 1884, 18, 179; Kohlrausch and Hallwachs, Ann. Physik, 1893, 50, 118; 1894, 53, 14; Kohlrausch, *ibid.* 1895, 56, 185; Traube, Ueber den Raum der Atome, Ahrens' Sammlung, 1899, 4, 255). The value of the molecular solution volume for a non-electrolyte in aqueous solution does not vary much, as a rule, with the concentration (*see* also Wanklyn, Chem. News, 1892, 65, 122). For an electrolyte, on the other hand, the molecular solution volume diminishes as the concentration of the solute diminishes and, in many cases at least, approaches a constant value in very dilute solution. From these values, Traube has deduced figures which represent the atomic solution volumes and he finds that for a non-electrolyte in aqueous solution the molecular solution volume is equal to the sum of the atomic volumes, *plus* an increment of 12·4 c.c., which is termed the 'molecular co-volume.' He further concludes that the contraction accompanying the dissolution of a gram-molecule of any non-electrolyte in water (a *dilute* solution being formed) is 13·5 c.c. at 15°, and that the contraction for each gram-ion of a binary electrolyte is the same as that for the gram-molecule of a non-electrolyte.

Osmosis and related properties. If a layer of concentrated sugar solution is put at the bottom of a tall jar and the jar is then carefully filled up with water, diffusion sets in, with the result that the concentration of the sugar ultimately becomes uniform throughout the jar. The existence of the force which thus brings about the intermixture of the sugar and the water could be rendered evident by interposing between solution and solvent some surface which would differentiate between sugar and water, preventing the passage of the former, but freely permeable to the latter. If a membrane with these properties were interposed between the water and the strong sugar solution the system would seek to reach equilibrium in the only way left open to it, viz. by water entering the solution through the membrane; that is, a one-sided diffusion, or 'osmosis,' would occur. The resulting increase in the bulk of the solution would lead either to the bursting of the membrane or, if the membrane were rigid and strong enough, to the production of a hydrostatic pressure opposing the further passage of water into the solution. The pressure developed in the solution in the latter case might be taken as a measure either of the driving force under the influence of which the sugar molecules diffuse; or, simply, of the attraction between solvent and solution.

These conditions are capable of experimental realisation. Membranes are known which may be described as 'semi-permeable,' since they are freely permeable to water, but impermeable to certain dissolved substances. A membrane of copper ferrocyanide, for instance, produced at the common surface of solutions of copper sulphate and potassium ferrocyanide, is permeable to water, but impermeable to dextrose or sucrose, and has been much used in the quantitative study of osmosis. When the copper ferrocyanide is deposited in the walls of a porous porcelain pot, sufficient strength and rigidity are imparted to the membrane to enable it to withstand high pressures. The porous pot, connected with a closed mercury manometer, is filled with a solution of dextrose or sucrose, and is then immersed in pure water. The force with which water seeks to enter the solution is then determined by measuring the pressure developed within the cell—the 'osmotic pressure,' as it is called.

The first direct determinations of this force (Pfeffer, Osmotische Untersuchungen, 1877) showed that the osmotic pressure of sucrose solutions at a constant temperature is approximately proportional to the concentration, and that the osmotic pressure of a given sucrose solution varies nearly as the absolute temperature (*see* van 't Hoff, Phil. Mag. 1888, 26, 81; Ladenburg, Ber. 1889, 22, 1225; Adie, Chem. Soc. Trans. 1891, 59, 344; König and Hasenbäumer, Zeitsch. angew. Chem. 1909, 22, 1009, 1070). The validity of these relationships has recently been subjected to a searching investigation by Morse, Frazer and others (Amer. Chem. J. 1905, 34, 1; 1906, 36, 1, 39; 1907, 37, 324, 425, 558; 38, 175; 1908, 39, 667; 40, 1, 194; 1909, 41, 1, 257; 1911, 45, 91, 237, 383, 517, 554). Working with dextrose and sucrose solutions containing from 0·1 to 1·0 gram-molecule per 1000 grms. of water, these investigators find that the osmotic pressure is proportional to the concentration, provided that this latter is referred, not to unit volume of the solution, but to unit volume of the solvent. For the temperature range 0°–25°, they find that the osmotic pressure of a given solution is proportional to the absolute temperature.

Direct determinations of the osmotic pressure of strong solutions have been made by Lord Berkeley and co-workers (Phil. Trans. A, 1906, 206, 481; 1909, 209, 177, 319; *see* also Proc. Roy. Soc. A, 1909, 82, 271). They have investigated sucrose solutions containing up to 750 grms. sucrose per litre and measured osmotic pressures up to 133 atmospheres. It is found that the osmotic pressure increases more rapidly than the concentration, even when the latter is referred to unit volume of the solvent. (For a summary of this work on osmotic pressure, *see* Lowry, Science Progress, 1913, 7, 544.)

For the purpose of finding 'isotonic' solutions—that is, solutions of equal osmotic pressure—a study of the water exchange taking place across a semipermeable membrane of animal or vegetable origin has been found useful (*see*, for instance, Tammann, Ann. Physik, 1888, 34, 299; de Vries, Zeitsch. physikal. Chem. 1888, 2, 415; Hamburger, *ibid.* 1890, 6, 319; Hedin, *ibid.* 1895, 17, 164). One chief result of these investigations has been to show that, for equal molecular concentrations, the osmotic activity of a binary salt (*e.g.* sodium chloride) is much greater than that of a non-electrolyte such as sucrose, and that ternary salts (*e.g.* calcium chloride) are still more active.

The vapour pressure p' of a solution of a non-volatile solute is lower than the vapour pressure p of the pure solvent at the same temperature, and the relation between these and the concentration is expressed by the formula $\frac{p-p'}{p}=\frac{n}{n+N}$, where n and N are the numbers of solute and solvent molecules respectively in the solution (*see* Raoult, Zeitsch. physikal. Chem. 1888, 2, 353). There is also a quantitative relationship between the osmotic pressure of a solution and its vapour pressure (van 't Hoff, *ibid.* 1887, 1, 481; Gouy and Chaperon, Ann. Chim. Phys. 1888, 13, 124; Arrhenius, Zeitsch. physikal. Chem. 1889, 3, 115; Berkeley and Hartley, Proc. Roy. Soc. A, 1906, 77, 156; Spens, *ibid.* 234; Porter, *ibid.* 1907, 79, 519; 1908, 80, 457). In order to deduce osmotic pressure from vapour pressure by this relationship it is necessary to know only the *ratio* of the vapour pressures of solvent and solution at the same temperature, not their absolute values. The value of the ratio can be found by Ostwald and Walker's method (Zeitsch. physikal. Chem. 1888, 2, 602), and Berkeley and Hartley, using a modified form of apparatus, have found that the values of the osmotic pressure deduced from the relative vapour pressures of solvent and solution are in good agreement with the values obtained by direct measurement (Proc. Roy. Soc. A, 1906, 77, 156; Phil. Trans. A, 1909, 209, 177).

The boiling point of a solution of a non-volatile solute is higher than that of the pure solvent, the extent of the rise being proportional to the molecular concentration of the solute (Raoult, Compt. rend. 1878, 87, 167; Beckmann, Zeitsch. physikal. Chem. 1889, 4, 532; 1890, 6, 437; 1891, 8, 223; 1894, 15, 656; compare, for other practical methods of finding the rise of boiling point for a solution: Sakurai, Chem. Soc. Trans. 1892, 61, 989; Landsberger, Ber. 1898, 31, 458; Walker and Lumsden, Chem. Soc. Trans. 1898, 73, 502; Turner, *ibid.* 1910, 97, 1184). For each solvent there is a characteristic figure or constant, known as the 'molecular elevation of the boiling point,' which is defined as the rise of boiling point for a solution containing 1 gram-molecule of solute in 100 grms. of solvent. This constant can be evaluated either empirically, from the rise of boiling point observed with normal solutes of known molecular weight, or from van 't Hoff's formula $k=0{\cdot}02T^2/l$, where T is the boiling point of the solvent on the absolute scale, and l is its latent heat of vaporisation.

The osmotic pressure P of a moderately dilute solution can be calculated from its boiling point T by the formula $P=\frac{1000Sl}{24{\cdot}25}\cdot\frac{T-T_0}{T_0}$ atmospheres, where S is the sp.gr. of the solvent at its boiling point T_0, and l is the latent heat of vaporisation for 1 grm. of solvent. For aqueous solutions this formula reduces to $P=56{\cdot}8\ (T-T_0)$ atmospheres.

The freezing point of a solution is lower than that of the pure solvent by an extent which is proportional to the molecular concentration of the dissolved substance (for details of this, *see* CRYOSCOPY). The osmotic pressure P of a solution is quantitatively related to its freezing point T by the formula $P=\frac{1000Sw}{24{\cdot}25}\cdot\frac{T_0-T}{T_0}$ atmospheres, where S is the sp.gr. of the solvent at its freezing point T_0, and w is the latent heat of fusion for 1 grm. solvent. For aqueous solutions this formula becomes $P=12{\cdot}03\ (T_0-T)$ atmospheres.

The quantitative relationships already referred to between osmotic pressure, lowering of vapour pressure, rise of boiling point, and depression of freezing point, on the one hand, and molecular concentration on the other, are, generally speaking, valid only for solutions of non-electrolytes. For electrolytic solutions, notably those of salts in water, the osmotic value, determined directly or indirectly, is abnormally high. The observed depression of freezing point, for instance, for a dilute solution of sodium chloride in water is nearly twice as great as the depression calculated from the accepted freezing point constant for water, on the assumption that the molecular condition of the dissolved salt is represented by NaCl. If $i=\frac{\text{observed depression}}{\text{theoretical depression}}$, it is found that for dilute solutions of binary salts such as sodium chloride or potassium nitrate, the values of i run up to 2, while for dilute solutions of ternary salts such as calcium chloride or sodium sulphate, the values run up to 3 (*see* Arrhenius, Zeitsch. physikal. Chem. 1887, 1, 635; 1888, 2, 495; Bedford, Proc. Roy. Soc. A. 1910, 83, 454). It is noteworthy that for solutions of sodium mellitate a value of i almost equal to 6 has been recorded (Taylor, Zeitsch. physikal. Chem. 1898, 27, 361).

Electrical conductivity. The significance of this property in relation to the constitution of solutions is generally admitted. The accurate determination of the electrical conductivity of aqueous salt solutions dates from the investigations of Kohlrausch (Ann. Physik, 1879, 6, 1, 145; 1885, 26, 161; *see* especially Kohlrausch and Holborn, Leitvermögen der Elektrolyte, 1898, where there is a full list of references to all the fundamental work on the subject). These, supported by the work of later investigators, have shown that whilst for a given salt the conductivity referred to standard dimensions of the conducting column diminishes as the dilution increases, on the other hand the conductivity referred to a fixed quantity of the dissolved salt *increases* with the dilution. The 'specific resistance' of an electrolytic solution is now defined as the resistance in ohms between two opposite faces of a centimetre cube containing the solution. The 'specific conductivity,' represented by the symbol κ, is the reciprocal of the specific resistance, and diminishes as the dilution increases. A measure of the conductivity referred to a fixed quantity of the dissolved electrolyte is given by the product $\kappa\times\phi$, where ϕ is the volume of solution (in cub. cm.) containing 1 gram-equivalent of the solute. The product $\kappa\times\phi$ is represented by the symbol Λ (or λ) and is termed the 'equivalent conductivity.' The equivalent conductivity of a salt (acids and bases included) increases as the concentration diminishes, and approaches a maximum limit at very high dilutions. In many cases at least, an extrapolation may be made and the limiting value Λ_∞ of the equivalent conductivity at infinite dilution thus obtained (*see* Kohlrausch, Ann. Physik, 1885, 26, 161; Bredig, Zeitsch. physikal. Chem. 1894, 13, 191). The variation of specific and equivalent conductivity with dilution for non-aqueous solutions appears to be generally of the same character as for aqueous solutions (*see* Walden, *ibid.* 1906, 54, 133; 1911, 78, 257; Turner, Amer. Chem. J. 1908, 40, 571; Dutoit and Duperthuis, J. Chim. phys. 1908, 6, 703; Philip and Courtman, Chem. Soc. Trans. 1910, 97, 1261).

The values of Λ_∞ for aqueous solutions, more particularly those of binary electrolytes, were shown by Kohlrausch to be additive in character; that is, Λ_∞ may be represented as the sum of two other values, attributable to the positive and negative ions respectively. The equation $\Lambda_\infty=u+v$, where u is the contribution of the cation and v is that of the anion, is the algebraic expression of Kohlrausch's Law of the Independent Migration of the Ions, for it is found that the contribution which any ion makes to the equivalent conductivity at infinite dilution is independent of the other ion with which it is associated (*see* Kohlrausch, *l.c.*; Loeb and Nernst, Zeitsch. physikal. Chem. 1888, 2, 948). The actual values of u and v are obtained by a combination of the figures for Λ_∞ and Hittorf's transport numbers (Pogg. Ann. 1853, 89, 177; 1856, 98, 1; 1858, 103, 1; 1859, 106, 338, 513; reprinted in Ostwald's Klassiker der exakten Wissenschaften: *see* also Loeb and Nernst, *l.c.*; Drucker, Zeitsch. Elektrochem. 1907, 13, 81; Kohlrausch, *ibid.* 333; McBain, Proc. Wash. Acad. Sci. 1907, 9, 1; Washburn, Technology Quart. 1908, 21, 164; Denison, Trans. Faraday Soc. 1909, 5, 165). The relation between the conductivity and the viscosity of salt solutions has also an important bearing on their constitution (*see* Kohlrausch, Sitzungsber. K. Akad. Berlin, 1902, 572; Bousfield and Lowry, Proc. Roy. Soc. 1902, 71, 42; Walden, Zeitsch. physikal. Chem. 1906, 55, 207; 1911, 78, 257).

Theories of solution. The remarkable way in which physical and chemical conceptions of the relation between solute and solvent have long struggled for pre-eminence has been sketched in detail by Walden (Ahrens' Sammlung, vol. 15: 'Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge'). The last three decades have witnessed a renewed activity in the investigation of solutions, resulting in the accumulation of a vast amount of material, some part of which has been indicated in the preceding paragraphs. Some scientists have interpreted these facts in terms of a chemical interaction of solute and solvent: by others physical considerations have been put in the foreground, to the exclusion of any chemical factor.

The 'hydrate' theory is based on the view that the formation of an aqueous solution is essentially a process of association, and that the solution contains compounds of solute and solvent, the complexity of which increases with dilution. The supporters of this theory originally found evidence for their views in the character of the density-concentration curves (*see* Mendeléeff, Zeitsch. physikal. Chem. 1887, 1, 273; Chem. Soc. Trans. 1887, 51, 778; Pickering, *ibid.* 1890, 57, 64; Watts' Dictionary, 1894, 'Solution,' second article). The method, however, adopted for deducing the composition of the definite hydrates supposed to be present in the solutions has been subjected to serious criticism, and in its original form the theory is hardly tenable. If modified in harmony with the conceptions of reversibility and mass action a hydrate theory of solution has many facts in its favour (*see* Lowry, Science Progress, 1908, 3, 124). The case in support of the view which regards the solvent as exercising an associative function has been stated also by Armstrong (Proc. Roy. Soc. A, 1906, 78, 264; *ibid.* 1908, 81, 80; Chem. News, 1911, 103, 97).

More generally accepted at the present time and more commonly employed as a working hypothesis in the investigation of solutions are the theories associated with the names of van 't Hoff and Arrhenius. By a thermodynamical argument, based on the validity of Henry's Law, van 't Hoff reached the conclusion that the osmotic pressure of a dilute solution must be proportional (1) to the concentration of the solute and (2) to the absolute temperature (Zeitsch. physikal. Chem. 1887, 1, 481; Phil. Mag. 1888, 26, 81; compare Rayleigh, Nature, 1897, 55, 253; Kelvin, *ibid.* 272; Larmor, *ibid.* 545). He pointed to Pfeffer's measurements (see above) as an experimental verification of these conclusions, and therefore felt justified in extending Boyle's Law and Gay-Lussac's Law to dilute solutions. Further, van 't Hoff extended Avogadro's hypothesis to solutions and assumed that at a given temperature equal volumes of two dilute solutions which have equal osmotic pressures contain the same number of dissolved molecules. Evidence in favour of this extension of Avogadro's hypothesis was found in the known influence of different substances on the vapour pressure and freezing point of a solvent. In analogy then with the gas equation $pv = RT$, the behaviour of substances in dilute solution may be represented by an equation $PV = R'T$, where P is the osmotic pressure and V is the volume of solution containing 1 gram-molecule of solute. The known values of P, V, and T, for dilute sucrose solutions showed that $R' = R$, and hence van 't Hoff concluded that the osmotic pressure of a dilute sugar solution is equal to the pressure which the sugar would exert if it were in the gaseous state at the same temperature and occupied the same volume as the solution. While this statement is valid for dilute solutions it is not strictly accurate for higher concentrations. Under these conditions the observed osmotic pressure for sucrose solutions is greater than the corresponding gas pressure, even when the concentration is referred to unit volume of solvent instead of unit volume of solution (*see* Morse and others, Amer. Chem. J. 1911, 45, 554; Berkeley and Hartley, Phil. Trans. A, 1906, 206, 481; Berkeley, Proc. Roy. Soc. A, 1907, 79, 125; Callendar, *ibid.* 1908, 80, 466).

It should be noted that the quantitative relationships involved in van 't Hoff's theory are independent of the exact way in which the osmotic pressure originates. Indeed, diverse views are held as to the origin and mechanism of osmotic pressure (*see*, for instance, Bredig, Zeitsch. physikal. Chem. 1889, 4, 444; L. Meyer, *ibid.* 1890, 5, 23; van 't Hoff, *ibid.* 1890, 5, 174; Ber. 1894, 27, 6; Whetham, Nature, 1896, 54, 571; Poynting, *ibid.* 55, 33; Armstrong, *ibid.* 55, 78; Barmwater, Zeitsch. physikal. Chem. 1899, 28, 115; Lowry, Kahlenberg and others, Trans. Faraday Soc. 1907, 3, 14; Traube, Ber. 1909, 42, 86).

In his original paper, van 't Hoff drew attention to the fact (see above) that there are certain substances which in aqueous solution give abnormally high osmotic pressures and the behaviour of which cannot be represented by the formula $PV = RT$. These exceptional cases are very numerous, but can be brought into line with normal substances by assuming that the abnormal substances are dissociated. Arrhenius had pointed out that it is precisely those substances (viz. salts, acids and bases) which give abnormally high osmotic values in aqueous solution that make water a conductor of the electric current, and he proposed a common explanation for the two phenomena by suggesting that when a salt is dissolved in water it dissociates to a greater or less extent into positively and negatively charged particles or ions. Such a dissociation would mean an increased number of units in solution and so would account for the abnormally high osmotic values observed with salt solutions. The presence of the ions would confer on the water the power of conducting the electric current, the passage of the current through a conductor of this kind being supposed to consist in the streaming of positive ions in the one direction and of negative ions in the other, under the influence of the applied E.M.F.

In relation to conduction, Arrhenius classified the molecules in a salt solution as active or inactive, according as their ions were independent in their movements or were closely linked together. Only the active molecules were able to take part in the conduction of the current, but it was supposed, in view of the variation of equivalent conductivity with concentration, that at extreme (infinite) dilution all the molecules of the dissolved salt became active. On this basis, a measure of the extent of dissociation in any salt solution is obtained by comparing the value Λ of the equivalent conductivity for that solution with the value Λ_∞ of the equivalent conductivity at infinite dilution. If α is the 'degree of dissociation' (or 'coefficient of ionisation') then $\alpha = \frac{\Lambda}{\Lambda_\infty}$. On the other hand, if i is a measure of the osmotic abnormality (see above), it follows that $\alpha = \frac{i-1}{n-1}$, where n is the number of ions into which a molecule of solute dissociates. Arrhenius was able to show that the values of α deduced for a given salt by the two independent methods were in fair, although not perfect, agreement (Arrhenius, Zeitsch. physikal. Chem. 1887, 1, 631; 1888, 2, 495; Watts' Dictionary, 1894, 'Solution,' first article; Whetham. Proc. Roy. Soc. 1900, 66, 192; Noyes, Technology Quart. 1904, 17, 293; Drucker, 'Die Anomalie der starken Electrolyte,' Ahrens' Sammlung, 1905; Bedford, Proc. Roy. Soc. A, 1910, 83, 454).

The electrolytic dissociation theory of Arrhenius has proved very serviceable in the quantitative study of numerous phenomena exhibited by aqueous solutions of acids, bases and salts; as, for instance, in the interpretation of diffusion (Nernst, Zeitsch. physikal. Chem. 1888, 2, 613; 1889, 4, 129; Arrhenius, *ibid.* 1892, 10, 51), of the relative strength of acids and bases (Ostwald, *ibid.* 1888, 2, 36, 270; van 't Hoff and Reicher, *ibid.* 779; Arrhenius, *ibid.* 1889, 4, 226; Walker, *ibid.* 319; Shields, Phil. Mag. 1893, 35, 365), of the influence of salts on the activity of the corresponding acids (Arrhenius, Zeitsch. physikal. Chem. 1888, 2, 284; 1890, 5, 1), of reciprocal solubility influences (Nernst, *ibid.* 1889, 4, 372; Noyes and others, *ibid.* 1890, 6, 241; 1892, 9, 603; 1898, 27, 267, 442), of the distribution of an electrolyte between two immiscible solvents (Nernst, 1891, 8, 110), and of the thermo-chemistry of salt solutions (Arrhenius, Zeitsch. physikal. Chem. 1889, 4, 96; 'Theories of Chemistry,' 1907, chap. xiii.).

The fact that water is such a good dissociating or ionising solvent is probably connected with its high dielectric constant (Thomson, Phil. Mag. 1893, 36, 320; Nernst, Zeitsch. physikal. Chem. 1894, 13, 531; Walden, *ibid.* 1906, 54, 129; compare Crompton, Chem. Soc. Trans. 1897, 71, 925; Dutoit and Friderich, Bull. Soc. chim. 1898, 19, 321; Dutoit and Aston, Compt. rend. 1898, 125, 240; Brühl, Zeitsch. physikal. Chem. 1898, 27, 319). This, however, does not adequately explain the cause of ionisation, or indicate the source whence the energy necessary for ionisation is derived. It has been growingly felt that in the earlier presentation and applications of the theory of electrolytic dissociation the part played by the solvent was too much neglected, and at the present time the view is commonly held that, in many cases at least, the ions of a salt solution are hydrated. Not only so; it is urged by some that it is the hydration of the ions which is the source of energy in ionisation (*see* Lowry, Science Progress, 1908, 3, 202). The evidence bearing on the existence of hydrated ions and the methods available for determining the extent of hydration have been summarised by Washburn (Technology Quart. 1908, 21, 360).

J. C. P.

SOMATOSE. An albumose preparation from meat.

SOMBRERITE. A mixed calcium and aluminium phosphate occurring on Sombrero and other islands of the Antilles (*v.* FERTILISERS; also PHOSPHORUS).

SOMNOFORM *v.* SYNTHETIC DRUGS.

SOPHORA JAPONICA (Linn.). This is a large and beautiful tree, not unlike an acacia, belonging to the *Leguminosæ*, which grows abundantly throughout China.

The undeveloped flower buds constitute an important yellow dyestuff employed by the Chinese for colouring the silken vestments of the mandarins. For this purpose the buds are collected and dried rapidly, either in the sun or by artificial means, usually with the addition of a little chalk. The method of dyeing consists in simply boiling for 1–1½ hours in a decoction of the flower buds, silk which has been previously mordanted by steeping overnight in a decoction of alum. Less frequently it is employed in the dyeing of cotton and wool. Its price is about 30*s.* a cwt.

This dyestuff has been studied by many chemists, especially by Schunck (Chem. Soc. Trans. 1888, 53, 262; 1895, 67, 30), who has proved that the glucoside which it contains formerly called sophorin (Förster, Ber. 1882, 15, 214) is in reality identical with rutin, the quercetin glucoside first isolated from rue (*Ruta graveolens* [Linn.]) by Weiss (Chem. Zentr. 1842, 903). (Compare also Stein, J. pr. Chem. [i.] 58, 399; 85, 351; 88, 280; Schunck, Manchester Memoirs, 1858, 2 ser. 15, 122.)

When applied to wool the *Sophora Japonica* buds give colours somewhat like those obtained with quercitron bark, viz. a dull orange with chromium, a yellow of moderate brilliancy with aluminium, a bright yellow with tin and a dark olive with iron. In dyeing power it seems to be equal if not slightly superior to quercitron bark, and is to be regarded as an excellent dyestuff, quite equal to those of similar character in general use (Hummel and Perkin, J. Soc. Chem. Ind. 1895, 458).

A. G. P.

SORANJES, or **SURANJI**, *v.* AAL.

SORBITE. One of the constituents of steel. It is intermediate in properties between cementite and pearlite (*q.v.*), and may be regarded as pearlite in which the lamellæ or granules are so fine that no microscope can resolve them (Osmond, Revue de Métallurgie, 1904).

It is an important constituent of structural steels, *v.* METALLOGRAPHY.

SORBITOL *v.* CARBOHYDRATES.

SORBOSE *v.* CARBOHYDRATES.

SOUDAN BROWN *v.* AZO- COLOURING MATTERS.

SOY. A well-known sauce made from soy beans (*Soja hispida* (Moench.); nat. ord. *Leguminosæ*), chiefly in Japan, and to a less extent in China, India, and the Moluccas. It is known to the Japanese as 'Sho-ju,' and to the Dutch, by whom it appears to have been introduced into Europe, as 'shoya.'

To prepare the sauce, the beans are ground up with an equal quantity of wheat or barley, and boiled with water until soft, when the mixture is left in a warm place for about 24 hours to ferment. It is then covered with a thick layer of salt, water poured over it, and the mass stirred daily for about a couple of months. The liquor is then poured off, squeezed out of the sediment and stored in wooden vessels, in which it clears on standing.

A Chinese sauce, known as 'kit-jap' (hence 'ketchup'), is sometimes sold as 'soy,' and often the article described under this name is nothing more than diluted molasses flavoured to imitate soy.

J. C.

SOYA (*Soja*) **BEAN OIL** (*Soy-Bean oil, Bean oil, Chinese Bean oil*). This oil is obtained from the seeds of *Glycine Soja*, Sieb. et Zucc., *Dolichos Soja*, Linn., *Soja hispida*, Moench, *Soja japonica* Savi, *Glycine hispida*, Maxim (' Sachuca bean '), a plant indigenous to China, Manchuria, Korea, Japan, Formosa, and Indo-China, where the oil and the expressed cake are largely used as foodstuffs. The seeds contain 18 p.c. of oil and about 30–40 p.c. of proteins.

The cultivation of the soya bean has been for centuries the main agricultural industry of Manchuria, and the industries based on the production of soya bean oil and soya bean cake have formed the most important manufacture of Manchuria, and to a large extent of Japan.

Up to the last Russian-Japanese war, the soya bean and soya bean oil were practically unknown in Europe. Since then, however, enormous quantities have been imported into Europe and the oil has in an extremely short time acquired the position of one of the foremost oleaginous seeds, rivalling in extent and importance the cotton-seed oil industry of Europe. Owing to their high proportion of proteins, they have rapidly acquired great commercial importance; especially so as it is stated that the soya cake is instrumental in producing cow-milk richer in butter fat than is obtained when feeding with linseed and cotton-seed cake. In this country, however, the cake has not yet been employed for feeding milk cows to the same extent that it has on the Continent (Denmark, Holland).

In Manchuria, three varieties of Soja are known, commercially, namely, yellow, green and black, but the commercial seeds represent at least seven varieties. The almost phenomenal importance which the soya bean industry has acquired in the course of two years has led to the attempt to cultivate the soya bean for commercial purposes in other countries, and at present experiments are being made to produce soya beans in Australia, South Africa, United States of America, Italy, Spain, South America, and even in this country.

In Manchuria, the beans are soaked in water over night, then crushed and boiled with a little water so as to burst the oil cells. The oil is then expressed in the most primitive fashion; but owing to the long time the cakes are allowed to remain in the press the yield of oil amounts to 13 p.c., whereas experiments made with modern machinery are stated to have yielded no more than 10 p.c. The expressed meal is made into bean-cakes which constitute one of the staple foods of the country, and form the most important article of export. Before the Russian-Japanese war, the chief export of beans from Manchuria was directed to Japan, where the bean is used on the most extensive scale for the preparation of the condiment 'Shoyu' and 'Misu' (Soja sauce).

For the characteristics of soya bean oil *see* OILS, FIXED, AND FATS.

The oil must be classed with the drying oils, inasmuch as it (or at least some varieties of the soya bean oil) yields up to 5 p.c. of hexabromide in the bromide test. The drying powers are, however, weak as compared with linseed oil.

J. L.

SOZAL *v.* SYNTHETIC DRUGS.

SOZOIODAL *v.* SYNTHETIC DRUGS.

SPANISH GRASS *v.* ESPARTO and PAPER.

SPANISH OCHRE. *Burnt Roman Ochre* *v.* PIGMENTS.

SPAR (Ger. *Spath*, *Spat*). A general term applied to a variety of minerals without metallic lustre which occur as crystals or which cleave into fragments with bright surfaces. Such sparry minerals are well known to miners as the gangue of metallic ores. Several kinds of spar are distinguished by popular names, and the term also enters into certain mineralogical names. For example: Derbyshire-spar (fluorspar); calc-spar, Iceland-spar, doubly-refracting spar, dog-tooth-spar, and nail-head-spar (calcite); heavy spar (barytes); satin-spar (gypsum and calcite); tabular spar (wollastonite); adamantine spar (corundum); felspar, feldspar; &c. In special trades, however, the term 'spar' is often used for one particular kind of spar.

L. J. S.

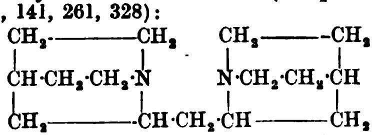
SPARTEINE $C_{15}H_{26}N_2$ (Mills, Chem. Soc. Trans. 15, 1) is the alkaloid of the common broom, *Cytisus Scoparius* (Link), in which it was discovered by Stenhouse (Chem. Soc. Trans. 4, 218). It is produced in greatest quantity during the early part of the life of the plant (Chevalier, Compt. rend. 1910, 150, 1068), and is prepared from broom-tops by adding caustic soda to the aqueous extract and then distilling with steam, or by evaporating the extract to dryness and dissolving out the alkaloid with dilute hydrochloric acid (Stenhouse). 1000 grms. of the plant yield 3 grms. pure product (Houdé, J. Pharm. Chim. [v.] 13, 39). For other methods of extraction *see* Houdé, *l.c.*; Kerchmann, Arch. Pharm. [iii.] 9, 209.

Sparteine is a thick, heavy liquid, colourless when freshly prepared, becoming brown on exposure to light and air. It boils at 180°–181° at 20 mm. (Bernheimer, Gazz. chim. ital. 13, 451); 287° (Houdé); 311°–311·5° at 723 mm. (Bamberger, Annalen, 235, 368); 326° (Wackernagel and Wolffenstein, Ber. 1904, 37, 3238); 188° (corr.) at 18·5 mm. and 325° (corr.) in a current of dry hydrogen at 754 mm. (Moureu and Valeur, Compt. rend. 1903, 137, 194). It has sp.gr. 1·034 at 0°, 1·0196 at 20° (Moureu and Valeur, *loc. cit.*), 1·0199 at 20° (Semmler, Ber. 1904, 37, 2428); the specific rotation $[\alpha]_D$ is $-16{\cdot}42°$ (M. and V.), $-14{\cdot}6°$ at 26° (Bernheimer, *l.c.*); and the refractive index n_D is 1·5293 at 19° (M. & V.), 1·5291 at 20° (Semmler).

It is soluble in water to the extent of 0·304 parts in 100 (Moureu and Valeur, *loc. cit.*), and is readily soluble in alcohol, ether, and chloroform; insoluble in benzene and petroleum (Houdé, *loc. cit.*).

Sparteine has a strong alkaline reaction and behaves as a diacid base towards phenol phthalein, &c., but as a monacid base to litmus. It has a very bitter taste and is a powerful narcotic poison. Administered in small doses (as the sulphate in aqueous solution) it strengthens the action of the heart and immediately regulates any disorder of the cardiac rhythm (Sée, Compt. rend. 101, 1046; *see* also Maurel, Compt. rend. Soc. Biol. 1903, 55, 1427, and Arch. Experim. Pathol. Pharm. 1892, 141).

Sparteine is a ditertiary base and is completely saturated; it does not contain methyl groups attached to nitrogen (Herzig and Meyer, Monatsh. 1895, 16, 599). On these and other grounds, the following formula has been proposed by Moureu and Valeur (Compt. rend. 1905, 141, 261, 328):



When oxidised with a strong solution of potassium permanganate or with silver oxide and water in sealed tubes it undergoes profound decomposition, among the products being pyridine, *a*-picoline and allied compounds (Peratoner, Gazz. chim. ital. 22, 566; Bernheimer, *ibid.* 13, 451; *cp.* Bamberger, Annalen, 235, 368). Hydrogen peroxide, however, converts it into *oxy-* and *dioxy- sparteine* (Ahrens, Ber. 24, 1095; 25, 3607; 26, 3035; 30, 195). The alkaloid *retamine*, obtained from the shoots and bark of *Genista* [*Retama*] *sphaerocarpa* (Lam.), is a hydroxy sparteine, $C_{15}H_{26}N_2O$, crystallising in long needles, m.p. 162° with decomposition (Battandier and Malosse, Compt. rend. 1897, 125, 360, 450; *see* also Willstätter and Marx, Ber. 1904, 37, 2351).

Tests for sparteine. Sodium picrate gives a yellow colour which on addition of sulphuric acid, ammonium persulphate and potassium thiocyanate turns orange-red. If the dry residue obtained by evaporating solutions of ferric chloride and potassium thiocyanate together be touched with a solution containing sparteine an intense bluish-violet colouration is obtained (Reichard, Pharm. Zeit. 48, 385).

Sparteine sulphate $C_{15}H_{26}N_2{\cdot}H_2SO_4,5H_2O$, prepared by dissolving the alkaloid in 10 p.c. sulphuric acid and allowing the solution to crystallise in a warm place, forms colourless rhombohedral crystals, soluble in 1·1 parts of water and in 2·4 parts of alcohol at 25°, insoluble in ether and chloroform. In aqueous solution at 15°–20° it has $[a]_D$ $-22{\cdot}12°$ (Moureu and Valeur, J. Pharm. Chim. 1903, [vi.] 18, 545).

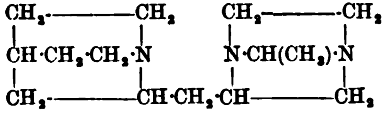
Sparteine hydrochloride and **hydriodide** are white crystalline solids, soluble in water; the latter has m.p. 226°–228°. The *platinichloride* $C_{15}H_{26}N_2{\cdot}H_2PtCl_6,2H_2O$ is yellow and decomposes at 244°–257°.

Sparteine picrate $C_{15}H_{26}N_2{\cdot}2C_6H_3O_7N_3$ has m.p. 208° (Moureu and Valeur, Compt. rend. 1903, 137, 194), 199°–200° (Wackernagel and Wolffenstein, *l.c.*).

Sparteine ferrichloride $C_{15}H_{26}N_2{\cdot}2HCl{\cdot}FeCl_3$ sinters at 190° (Scholtz, Arch. Pharm. 1909, 247, 534).

Sparteine ferrocyanide is a white crystalline solid, easily soluble in water (Beckurts, Arch. Pharm. 228, 347).

***iso*-Sparteine**



has been isolated by Moureu and Valeur (Compt. rend. 1907, 145, 1184, 1343).

Numerous derivatives of sparteine and *iso*-sparteine have been prepared: for an account of these the original papers must be consulted—

Dihydrosparteine (Ahrens, Ber. 20, 2218; 21, 825).

Oxysparteine (Ahrens, Ber. 24, 1095; 25, 3607; 26, 3035; 30, 195).

Hydroxysparteine $C_{15}H_{24}ON_2$ (Ahrens, *ibid.* 1905, 38, 3268).

Dehydrosparteine (Ahrens, *ibid.* 26, 3035).

Spartyrine $C_{15}H_{24}N_2$ (Willstätter and Marx, Ber. 1905, 38, 1772).

Ethylspartylammonium iodide $C_{15}H_{27}EtN_2I_2$ (de Coninck, Compt. rend. 104, 513).

Methyl-derivatives of *sparteine* and *iso-sparteine* (Moureu and Valeur, Compt. rend. 1905, 140, 1645; 141, 49, 117; 261, 328; 1907, 145, 815, 929, 1184; 146, 79; Moureu and Valeur, Bull. Soc. chim. 1908, [iv.] 3, 674; Compt. rend. 1908, 147, 127, 864, 1318; Valeur, Bull. Soc. chim. 1909, [iv.], 5, 31 *et seq.*).

SPATHIC IRON-ORE *v.* CHALYBITE.

SPEARMINT-OIL *v.* OILS, ESSENTIAL.

SPECIFIC GRAVITY. This term, taken strictly, means the ratio of the true weight of a given volume of a substance to the true weight of an equal volume of water at the same temperature *t*°C.; the ratio is frequently indicated by the symbol d^t_t. The correction for displaced air, however, is not always made, so that the value quoted for d^t_t often means the ratio of the *apparent* weights of equal volumes of substance and water at the same temperature. The higher the specific gravity of the substance, the greater is the difference in value between the two ratios, as just defined. In the case, for example, of a liquid with a specific gravity of 1·9, the difference would amount to 1 unit in the third place of decimals.

Again, 'specific gravity' is frequently taken to mean the ratio of the true weight of a given volume of a substance at temperature *t*° to the true weight of an equal volume of water at 4°: the ratio is frequently indicated by the symbol d^t_4. In view of the relation between weight and volume of water in the C.G.S. system it is evident that the specific gravity of a substance, as thus defined, has the same numerical value as its absolute density, which is the mass in grams of a cubic centimetre. It should be pointed out that the values of d^t_4 recorded in the literature often refer to the ratio of the *apparent* weights of equal volumes of the substance and water at *t*° and 4° respectively. The indefiniteness that prevails in the use of the term 'specific gravity' makes it desirable to indicate along with each recorded value (1) whether water at *t*° or water at 4° is taken as the standard of reference; (2) whether a correction has been made for displaced air.

The term 'specific gravity' is used mainly in connection with the densities of liquids and solids relatively to water. Gases are usually compared with air or hydrogen as a standard, and the 'relative density' of a gas means the ratio of the weight of a given volume of the gas at given temperature and pressure to the weight of an equal volume of air (or hydrogen) under the same conditions. Owing to the uniform influence of temperature on the volumes of different gases this ratio is independent of temperature; whilst, on the other hand, the relative density or specific gravity of a liquid, $d^t_{t'}$, is a variable figure.

In all determinations of specific gravity or density, the essential operation is to find the weight of a known volume of the substance at known temperature and, in the case of a gas, known pressure. In the following sections, an account is given of the chief methods used in such determinations.

DENSITY OF GASES AND VAPOURS.

The standard method for the accurate determination of the density of gases is the one employed originally by Regnault and perfected by later workers, notably von Jolly (Trans. Munich Acad. 1880, 13, ii. 49), Rayleigh (Proc.

Roy. Soc. 1893, 53, 134), Leduc (Compt. rend. 1891, 113, 186), and Morley (Smithsonian Contributions to Knowledge, 1895; Zeitsch. physikal. Chem. 1896, 20, 68, 242). The principle of the method may be suitably explained by reference to the apparatus used by Lord Rayleigh (*l.c.*). The glass globe S, which can be surrounded with ice in the inverted bell-jar T, contains about 1800 c.c. and is connected with the rest of the apparatus by a short piece of thick-walled indiarubber tubing U. The tube V communicates with the gas-generating apparatus and connection is made through the tap W with a Töpler pump X, and further, through the tube D, with the vacuum chamber of a special manometer. The side tube E leads to the pressure chamber of the same manometer.

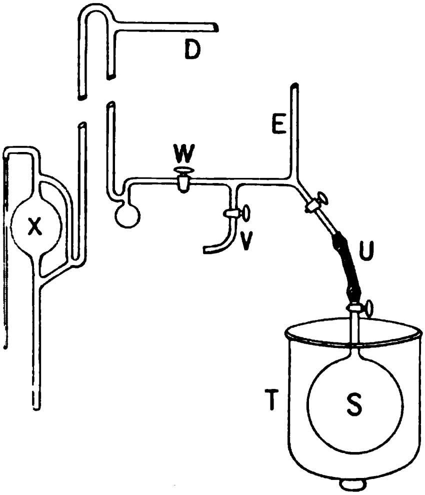


FIG. 1.

The volume of the globe is ascertained by finding the weight of boiled-out distilled water which it contains up to the top of the passage in the stopcock. After it has been dried it is attached to the rest of the apparatus as shown in Fig. 1. The globe is then alternately evacuated and filled with the gas under examination, its weight being determined between each operation. During the filling of the globe it is surrounded with ice, and before the stopcock is closed the pressure is read off on the manometer. The temperature and pressure of the gas filling the globe are thus accurately known. In order to eliminate the effects of changes in the temperature and pressure of the atmosphere, and therefore in the buoyancy of the displaced air, in the interval between the weighing of the vacuous globe and the weighing of the filled globe, a counterpoise must be employed. This should be a closed glass globe of the same external volume as the one already referred to. The 'dummy' globe, further, should be subjected to the same treatment, in regard to washing and wiping, as the working globe, so that the two glass surfaces, when the weighing is made, shall, as far as possible, be in the same condition. In the most accurate work it is necessary to make a correction, indicated by Lord Rayleigh, for the contraction which the globe undergoes when it is evacuated. In the case of a globe of 1800 c.c. capacity, this contraction amounts to about 0·43 c.c., and the air displaced by the vacuous globe is less by this amount than the air displaced by the full globe. The weight of 0·43 c.c. of air at the temperature and pressure of the balance case must therefore be added to the observed weight of the gas filling the globe.

The foregoing method, when applied with all due precautions, gives results of high accuracy. Successive determinations by Lord Rayleigh of the weight of oxygen filling his working globe under constant conditions gave figures the extreme variation of which was about 1 part in 9000, and this although the oxygen was obtained from different sources. Where the available supply of gas is small, and the use of large globes is therefore out of the question, the attainable accuracy is not so high. Travers has estimated that in the case of helium, for instance, with a globe of 30 c.c. capacity, it should be possible to determine the density to within 1 p.c. of the true value. A description of the apparatus used in finding the densities of the rare gases has been published by Ramsay and Travers (Phil. Trans. A, 1901, 197, 54).

The accurate determination of the densities of gases has assumed great importance in connection with certain atomic weight problems. When allowance is made for the extent to which the different gases deviate from strict adherence to Boyle's Law, that is, when the compressibility is taken into account, it is possible to deduce from the relative density of a gas found for a pressure of 760 mm. the value which it would have at an infinitely low pressure. It is then assumed that the molecular weights of different gases would be strictly proportional to such limiting densities (*see* D. Berthelot, Compt. rend. 1898, 126, 954, 1030, 1415, 1501; Rayleigh, Phil. Trans. A, 1905, 204, 351). The molecular weights so calculated were in harmony with the accepted atomic weights except in one case, viz. that of nitrogen. Here the application of the physical method of limiting densities has led to a revision of the atomic weight for this element (*see* Gray, Chem. Soc. Trans. 1905, 87, 1601; 1906, 89, 1173; Guye and others, Compt. rend. 1905, 140, 1386; 141, 826; J. Chim. phys. 1905, 3, 537; Ber. 1906, 39, 1470).

Schloesing's method for finding the relative density of a gas depends on certain well-known hydrostatic principles and can be used when only 5–10 c.c. of gas are available (*see* Compt. rend. 1898, 126, 220, 476, 896). Two long capillary tubes, arranged vertically and communicating at the bottom through a 3-way tap, with each other or with a mercury reservoir, are charged with air, carbon dioxide and a gas X of unknown density. The carbon dioxide (supposed to be the heaviest of the three gases) occupies the lower part of the tubes, while the upper parts are occupied by air and X respectively. When equilibrium has been established between the two tubes, the positions of the two surfaces air—CO_2 and CO_2—X will obviously depend on the relative densities of air and X. These positions can be determined by allowing mercury to rise into each tube separately and drive over the contents into an absorption vessel filled with caustic potash. The unabsorbed air or X is then brought back into its tube, and the position of the mercury at atmospheric pressure is read off. In this way, without weighing and without reading the barometer, the density of X can be deduced from the densities of air and carbon dioxide.

Another method for the determination of the densities of gases was devised by Bunsen, and depends on the rate of effusion through a minute hole in a thin plate of platinum. The densities of two gases are proportional to the squares of the times of effusion, so the experiment consists in determining the time occupied by the passage of a certain volume of air through the aperture, and then determining the time required for the effusion of the same volume of the gas. The density in relation to air is obtained by dividing the square of the number of seconds recorded in the second case by the square of the number found in the first.

Bunsen's apparatus, described in his Gasometry (1857, 121–127), has since been improved by Schilling, and in this form is employed for controlling the density of coal gas. The results given by this apparatus are reliable to about 1 part in 500. The Simmance-Abady specific gravity bell is used for a similar purpose and is based on the same principle. Effusion apparatus has been employed also in the study of the rare gases (Donnan, Phil. Mag. 1900, 49, 423; compare Emich, Monatsh. 1903, 24, 747; 1905, 26, 505).

The control of the density of coal gas, already referred to, is frequently effected with the help of a so-called gas balance. The characteristic part of such an apparatus is a hollow brass sphere which takes the place of one side of the beam, and which can be filled *in situ* with the gas under examination. On the other side, the beam carries a rider and ends in a pointer which moves in front of a vertical scale (*see* Lux, Zeitsch. anal. Chem. 1887, 26, 38; 1890, 29, 13; J. Soc. Chem. Ind. 1890, 9, 415).

When it is desired to ascertain the density in the state of vapour of a substance which is liquid under the ordinary conditions of temperature and pressure, special methods must be adopted.

In Dumas' method of determining vapour densities, the weight of a known volume of the vapour is determined. A light glass flask, of a capacity of from 100 to 350 c.c. (according to the density of the vapour to be determined), has its neck drawn out to a fine point and bent nearly at right angles (see Fig. 2). The flask has to be filled with dry air, which is done by connecting the point with a calcium chloride tube and attaching the latter to an air-pump. The flask is several times exhausted, and filled with air which has passed through the drying tube. The flask full of air is now weighed, the temperature and the barometer being simultaneously read. The end of the tube is next dipped into the liquid, or the fused substance, if the body of which the vapour density is to be determined is solid at the ordinary temperature, and by alternate heating and cooling some of the liquid is introduced into the flask. The flask is lowered into a bath of boiling water or of hot oil; the liquid boils, and its vapour expels the air. The introduction of the flask into the bath must be done with caution, for a dangerous pressure might be produced in the flask if the evaporation were too rapid. When the temperature of the bath is well above the boiling point of the liquid and vapour ceases to escape from the orifice, the point is sealed by a blowpipe flame, the temperature of the bath and the height of the barometer being observed at the same time. The flask is removed from the bath, cleaned, and weighed. The next process is to determine the capacity of the flask. For this purpose the point of the flask is broken under mercury, and the mercury is forced in by atmospheric pressure. If the mercury completely fills the flask it shows that no air was mixed with the vapour of the substance. The mercury is now poured out into a graduated vessel, and the quantity measured. This gives the volume of the vapour that the flask contained. If a bubble of air is observed above the mercury in the flask, its volume must be determined either by refilling the flask completely after measuring the mercury, or more conveniently by running mercury in from a burette until the flask is quite full of mercury with the condensed liquid above it; the volume of mercury thus introduced is equal to the volume of the residual air. The capacity of the flask is now determined by measuring the mercury as before described. The data are sufficient for the calculation of the vapour density; the weight of the flask is the weight first obtained *minus* the weight of the volume of air at the temperature and pressure at the time of weighing calculated from the volume of the flask found in the last operation. The weight of the vapour is the weight obtained in the second weighing *minus* the weight of the flask. The volume of the vapour at 0° and 760 mm. pressure is calculated from the volume of the flask and the temperature and pressure at the time of sealing, and the weight of an equal volume of air or of hydrogen is calculated from the known weights of a litre of these gases. A correction may be made for the increase of the capacity of the globe at the temperature at which it is sealed, but in most cases this correction is unnecessary. When Dumas' method is used the substance must be pure, for if it is a mixture the portions with the lower boiling point pass off first, and the density ultimately arrived at is vitiated by the presence of the substances of higher boiling point.

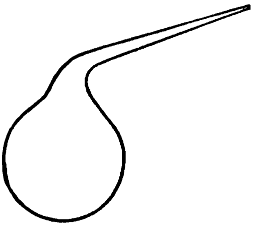


FIG. 2.

The original Dumas' method has been variously modified. Habermann suggested that the vaporisation in the bulb should be carried out under reduced pressure (Annalen, 1877, 187, 341). Less material is then required, and the bulb need not be heated beyond the ordinary boiling point of the substance. Minor modifications have been proposed by Pettersson and Ekstrand (Ber. 1880, 13, 1191), Pawlewski (*ibid.* 1883, 16, 1293), Schall (*ibid.* 1885, 18, 2068), Friedel and Crafts (Compt. rend. 1888, 106, 1764), Winkler (Chem. Zeit. 1899, 23, 627). For use at very high temperatures, the bulbs may be made of porcelain instead of glass (Deville and Troost, Ann. Chim. Phys. 1860, 58, 257).

Instead of determining the weight of a known volume of the gasified substance it is possible to start with a known weight of the liquid, the vapour density of which is to be ascertained, and then to find the volume occupied by this in the gaseous state at known temperature and pressure. This is the principle underlying Gay-Lussac's method, in which a small sealed bulb with a known quantity of the liquid under investigation was introduced into a graduated tube filled with mercury and standing in a bath of this metal. This tube was surrounded by a cylinder containing a suitable liquid, and by heating the mercurial trough the temperature was brought to such a point that the substance in the inner tube was completely gasified. Gay-Lussac's method was notably improved by Hofmann (Ber. 1868, 1, 198). The graduated tube was lengthened up to a metre, so that the substance vaporised into a vacuous space and the vapour produced was under a very small pressure. This fact made it possible to ascertain the vapour density of a substance at temperatures well below its boiling point. The tube, further, was jacketed with the vapour of a boiling liquid, such as aniline or water, and the use of small stoppered bottles was suggested instead of sealed bulbs.

Hofmann's method has been applied in various modified forms (*see* Brühl, Ber. 1876, 9, 1368; 1879, 12, 197; Thorpe, Chem. Soc. Trans. 1880, 37, 147; Capstick, Phil. Trans. A, 1894, 185, 1; Ramsay and Steele, Phil. Mag. 1903, 6, 492; Blackman, Ber. 1908, 41, 768, 4141) and is capable of giving results of high accuracy. The apparatus devised by Thorpe is shown in Figs. 3–5.

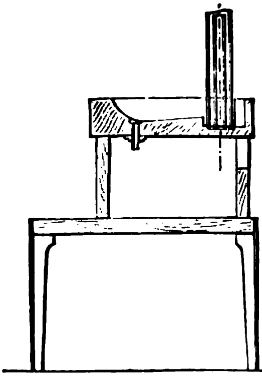


FIG. 3.—SECTION OF MERCURY TROUGH.

Instead of the barometer tube being graduated through its whole length, only one mark is etched on it near the closed end. The capacity of the closed end to the mark is first determined, and the rest of the tube is calibrated by pouring in known quantities of mercury as in calibrating a eudiometer, the levels of the mercury in the tube being read off on a graduated scale placed by its side. The mercury trough is provided with a shallow well in which the barometer tube and the surrounding cylinder stand, and there is an opening at the bottom of the other portion of the trough by means of which the mercury may be drawn through a caoutchouc tube into a tubulated bottle. Through the bottom of the trough and into the well pass two nickel-plated copper tubes, one of which passes to the bottom and the other to the top of a copper boiler placed below the level of the trough, and containing the liquid the vapour of which is to heat the barometer. When an experiment is to be made the two copper tubes are connected by a short india-rubber tube (to prevent the access of mercury), and the bottle of mercury raised so as to fill the trough. The calibrated tube is next filled with mercury and inverted in the trough, and the weighed substance introduced. The tube is placed in the well, the mercury run out from the trough, and the india-rubber tube removed from the copper tubes. A wide cylinder is now placed round the barometer tube so as to inclose the tubes connected with the boiler between the cylinder and the barometer, and to the top of the wide tube a cap is fitted connected to a vertical metal condenser, which also acts as the support of the glass tubes. The liquid in the boiler is now raised to ebullition, and the vapour which condenses in the cylinder returns to the boiler by the tube which passes to the bottom, and which is a little shorter than the other tube. Any vapour which passes through the cylinder is condensed by the vertical condenser and falls into a funnel attached to the return tube to the boiler. The mercury expelled from the barometer flows over the edge of the well, and runs into the bottle. In this form of apparatus the whole of the mercury in the barometer tube is uniformly heated, which renders it possible to make an accurate correction for the pressure. When the vapour ceases to expand, the lower end of the steel scale is brought in contact with the mercury in the well, and the level of the mercury in the tube is measured by moving downwards by rack and pinion a piece of brass which partly surrounds the wide tube. This gives the height of the column in the barometer, and, by reference to the calibration table, the volume of the vapour in the tube.

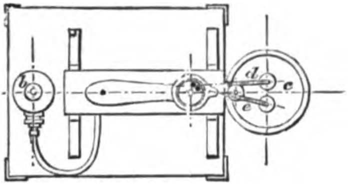


FIG. 4.—PLAN OF MERCURY TROUGH.

A more convenient, if less accurate, process for the determination of vapour densities was devised by V. Meyer (Ber. 1878, 11, 1867, 2253), and depends on the measurement of the volume of air expelled from a closed vessel by the volatilisation of a known weight of the substance. The apparatus (see Fig. 6) consists of a cylindrical bulb, B, of about 100 c.c. capacity, attached to the end of a long tube. Near the upper end of the latter a side-tube, D, is attached which dips downwards into a water trough, and over the end of this delivery tube a graduated cylinder, H, full of water may be placed, the top of the vertical tube being closed by a cork. At the bottom of the cylindrical bulb a quantity of asbestos is placed to prevent the fracture of the glass by the introduction of the vessel containing the substance under investigation. The bulb and part of the long tube are heated in the vapour of a liquid boiling at least 20° higher than the boiling point of the substance itself, or in a bath of molten lead. When the temperature of the tube becomes constant (indicated by the cessation of escape of air through the water in the trough) the graduated tube is placed over the end of the delivery tube, the cork withdrawn from the long tube, and a small vessel, containing a weighed quantity of the substance, is allowed to fall into the apparatus and the cork immediately replaced. Instead of falling directly to the bottom of the bulb B, the small vessel may be allowed to rest on a movable rod (see Fig. 6), until the cork has been replaced. The said vessel may be a small stoppered bottle or sealed bulb: in the latter case the capillary end of the bulb must be broken off before it is introduced into the apparatus. The volatile body is rapidly transformed into vapour, and air is expelled and collected in the graduated cylinder. The evaporation takes place so rapidly that none of the vapour has time to diffuse into the cooler parts of the apparatus, and the air expelled, when reduced to the normal temperature and pressure, is equal to the corrected volume of the vapour produced from the weighed quantity of the substance. From the data thus obtained the vapour density is calculated.

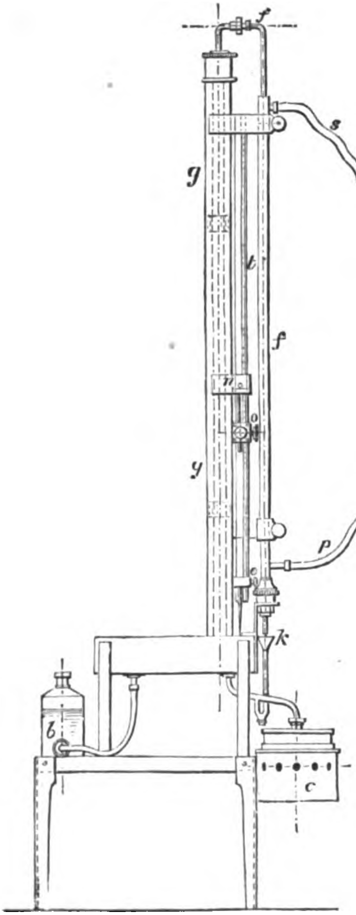


FIG. 5.

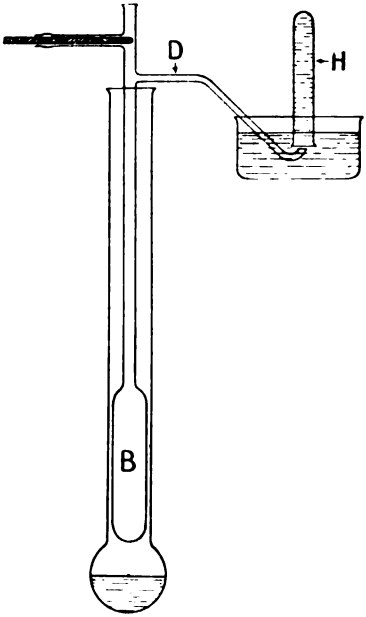


FIG. 6.

The air displaced from the apparatus may be collected and measured in a gas burette, instead of in a graduated tube over water, while the reduction to N.T.P. may be facilitated by using a Lunge gas volumeter (Lunge and Neuberg, Ber. 1891, 24, 729). This latter apparatus has the further advantage that it permits the determination of vapour density by V. Meyer's method under reduced pressure (*see* also Meunier, Compt. rend. 1884, 98, 1268; La Coste, Ber. 1885, 18, 2122; Schall, *ibid.* 1887, 20, 1827, 2127; Richards, Chem. News, 1889, 59, 39; Bodländer, Ber. 1894, 27, 2267). Various devices have been suggested which permit the introduction of the substance into the heated space without opening the apparatus (L. Meyer, Ber. 1880, 13, 991; La Coste, *l.c.*; Bott and Macnair, Ber. 1887, 20, 916; Biltz and V. Meyer, Zeitsch. physikal. Chem. 1888, 2, 189; Eykman, Ber. 1889, 22, 2754; Patterson, Chem. News, 1908, 97, 73).

In determining vapour density at atmospheric pressure by V. Meyer's method, the temperature of the bath should ordinarily be somewhat higher than the boiling point of the substance under examination; but Demuth and Meyer have shown (Ber. 1890, 23, 311) that if the apparatus is filled with hydrogen and provision is made for rapid diffusion and dilution of the vapour, the density may be satisfactorily determined at temperatures below the boiling point. If it is desired to find vapour densities at very high temperatures the apparatus must be made of some refractory material, such as platinum, porcelain or iridium (*see* V. and C. Meyer, Ber. 1879, 12, 1112; V. Meyer, *ibid.* 1880, 13, 394; Crafts, Compt. rend. 1880, 90, 183; Nilson and Pettersson, J. pr. Chem. 1886, 33, 1; Zeitsch. physikal. Chem. 1889, 4, 211; Biltz and Meyer, *ibid.* 1889, 4, 249; Biltz, *ibid.* 1896, 19, 385; Meyer and Recklinghausen, Ber. 1897, 30, 1926). For vapour density determinations in the neighbourhood of 2000°, Nernst uses a small iridium vessel, coated with magnesia and asbestos, in which 0·1–1·0 mg. of the substance under investigation is vaporised. The substance is weighed on a special micro-balance and the increase of volume due to vaporisation is measured by the displacement of a thread of mercury in a calibrated capillary tube (*see* Zeitsch. Elektrochem. 1903, 9, 622: also Löwenstein, Zeitsch. physikal. Chem. 1906, 54, 707; von Wartenberg, Zeitsch. anorg. Chem. 1907, 56, 320).

It is one of the advantages of V. Meyer's displacement method that the temperature at which vaporisation takes place need not be known. In certain cases, however, notably those in which the vapour density varies with temperature, it is desirable to know the temperature of vaporisation. This can readily be ascertained either by using the vapour density bulb itself as an air thermometer (Nilson and Pettersson, J. pr. Chem. 1886, 33, 1; Biltz and Meyer, Zeitsch. physikal. Chem. 1889, 4, 249), or by sweeping out and measuring the volume of some readily absorbed gas, such as carbon dioxide or hydrogen chloride, which fills the bulb at the temperature of observation (*see* Crafts and Meier, Compt. rend. 1880, 90, 606; Meyer and Züblin, Ber. 1880, 13, 2021; Mensching and Meyer, Zeitsch. physikal. Chem. 1887, 1, 145). In both these methods the uncertainty arising from the unequal temperature of the stem of the vapour density bulb is eliminated by the use of a 'compensator,' a blind tube of the same dimensions as the stem. The compensator is exposed to the same conditions as the stem, and the gas it gives up or contains is deducted from the corresponding volume for the stem + bulb.

As has been already pointed out, the vapour density of a substance may be deduced from the increase in volume due to the vaporisation of a known weight at constant pressure. It is equally possible to deduce the vapour density from the increase of pressure due to the vaporisation of a known weight at constant volume. Such a method of finding vapour density is based on the principle that equimolecular quantities of different substances, vaporised in a given space and at a given temperature, produce the same increase of pressure. Many forms of apparatus, based on this principle, some of them adapted for working under reduced pressure, have been proposed (Pfaundler, Ber. 1879, 12, 165; Dyson, Chem. News, 1886, 55, 88; Bott and Macnair, Ber. 1887, 20, 916; Schall, Ber. 1887, 20, 1435, 1759; 1888, 21, 100; 1889, 22, 140; 1890, 23, 919, 1701; Malfatti and Schoop, Zeitsch. physikal. Chem. 1887, 1, 159; Eykman, Ber. 1889, 22, 2754; Richards, Chem. News, 1889, 59, 87; Bleier and Kohn, Monatsh. 1899, 20, 505; Erdmann, Zeitsch. anorg. Chem. 1902, 32, 425; Lumsden, Chem. Soc. Trans. 1903, 83, 342; Haupt, Zeitsch. physikal. Chem. 1904, 48, 713; Blackman, Chem. News, 1909, 100, 13, 174). Fig. 7 shows the apparatus used by Bleier and Kohn. The vaporisation bulb A is connected with a manometer, B, and, through the stopcock *h*, with a pump. By adjusting the height of the reservoir R, the mercury in the right-hand limb of the manometer is brought to the same level *a* before and after vaporisation; the change of pressure due to vaporisation is read off on the left-hand limb. The fine adjustment of the mercury at *a* is effected by the screw clip *m*.

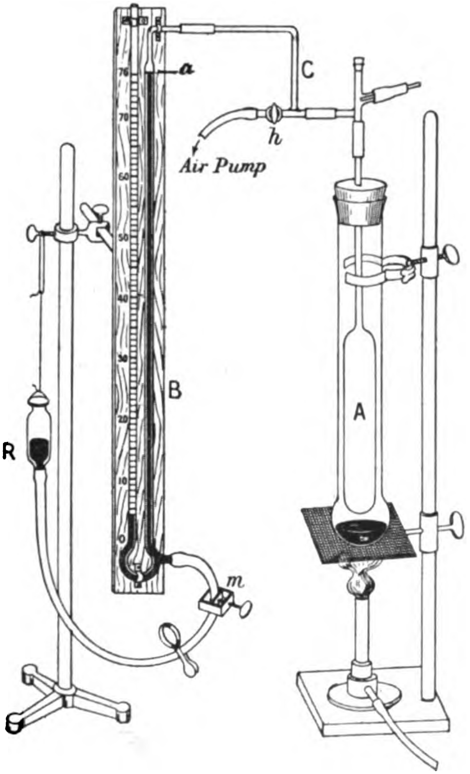


Fig. 7.

Density of Liquids.

One common way of finding the density of a liquid is to determine the mass of the liquid which exactly fills a vessel of known volume. The vessels usually employed for this purpose are known as specific gravity bottles and pyknometers. The simplest form of specific gravity bottle is a thin glass flask with a flat bottom and an accurately-fitting stopper, through which a fine hole is drilled (see Fig. 8). The dry, clean flask is carefully weighed and then filled with the liquid, the temperature being noted. The stopper is then placed in the neck, the excess of liquid escapes through the perforation in the stopper and is wiped off from the glass, and the flask is again weighed. The flask is now emptied, cleaned, filled with distilled water, and again weighed. If the temperature of the water is the same as that of the liquid at the moment of putting in the stopper, then the weight of the liquid (w) divided by the weight of the water (w') gives the relative density of the liquid to that of water at the particular temperature $t°$. If the absolute density is required, a correction must be made (1) for the quantity of air displaced by the liquids and the weights, (2) for the deviation of the density of the water from unity. If D is the absolute density of the liquid at $t°$, then $D=\frac{w}{w'}\Delta+\sigma\left(1-\frac{w}{w'}\right)$, where Δ is the density of water at $t°$, and σ is the density of the air at the time of the observations. In most cases it is sufficient to take $\sigma=0{\cdot}0012$, and a table may therefore be constructed giving the values of the correction term $\sigma\left(1-\frac{w}{w'}\right)$ for various values of the uncorrected density $\frac{w}{w}$. (For a discussion of these corrections *see* Wright, J. Soc. Chem. Ind. 1892, 11, 297; Wade and Merriman, Chem. Soc. Trans. 1909, 95, 2174.)

FIG. 8.

The specific gravity bottle just described is not free from objection, for evaporation takes place at the top of the perforated stopper, and further, if the temperature of the balance case is higher than the temperature at which the bottle was filled, there is an overflow. The first difficulty may be avoided by having a cap ground to fit the neck of the bottle (Louis, J. Soc. Chem. Ind. 1894, 13, 322). The second difficulty may be met by grinding into the neck of the flask a tube which is contracted in its middle to a capillary bore, and is provided at the top with a small reservoir closed by a stopper (Fig. 9). To use this modification, the flask is filled and the tube inserted. This forces a small quantity of the liquid through the capillary tube into the reservoir above. The flask is now placed in a bath of known temperature, or even in water at 4°, and left there until its temperature is constant. If the liquid contracts so as to empty the reservoir above the capillary tube, a small additional quantity is introduced. When no change of volume is perceptible, a thin piece of filter paper or a fine glass tube is introduced into the reservoir so as to reduce the level of the liquid to a mark, *a*, which is made on the outside of the capillary tube. The stopper may then be introduced into the reservoir, the flask removed from the bath and its outside dried, and it may now be left until it has reached the temperature of the balance case where it is to be weighed.

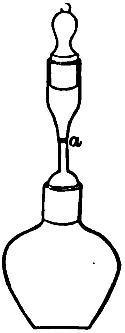


FIG. 9.

Various modifications of this form of specific gravity bottle have been suggested (*see* Squibb, J. Amer. Chem. Soc. 1897, 19, 111; Leimbach, J. pr. Chem. 1902, 66, 475; Bošnjaković, Zeitsch. anal. Chem. 1904, 43, 230). It has been proposed, too, that the capillary tube should be provided not with a single mark, but with regular graduations, the values of which are determined once for all (Tribe, Chem. News, 1873, 28, 211; Squibb, J. Amer. Chem. Soc. 1897, 19, 111; *see* also Louis, J. Soc. Chem. Ind. 1894, 13, 322).

The Sprengel pyknometer (Chem. Soc. Trans. 1873, 26, 577) is a U-shaped tube terminating in two capillary tubes bent in opposite directions (Fig. 10). The liquid is aspirated into the tube, which is then sunk in a beaker of water, the capillary tubes resting on the edge of the beaker. When the temperature of the contained liquid is constant, as shown by the cessation of movement of the liquid in the capillary tube, some of the liquid is removed from one capillary, which terminates in a fine point, *a*, by means of a piece of filter paper, until the liquid in the other capillary reaches a mark, *b*, near the bend. Should the amount of liquid in the pyknometer be insufficient a little is conveniently added by touching the point *a* with a drop held on the end of a glass rod. Sprengel's pyknometer was modified by Ostwald (J. pr. Chem. 1877, 16, 396), who made the limb of the U-tube next *b* of narrow-bore tubing throughout. In the case of volatile or hygroscopic liquids, it is advisable to close the ends of the capillaries, after the adjustment has been made, with glass caps.

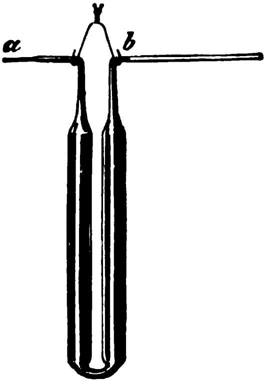


FIG. 10.

Immediate contact of the liquid with the air is avoided, and determination of the density at temperatures below that of the laboratory is made possible by Perkin's modification of the Sprengel pyknometer (Chem. Soc. Trans. 1884, 45, 443; 1896, 69, 1043). In this the narrow tubes are bent at obtuse angles instead of right angles, and a small bulb is blown on the tube adjoining the shorter limb (see Fig. 11). A mark, *a*, is made just below the small bulb, the other limb terminating in a fine opening at *b*. After the liquid has been introduced into the tube, the latter is immersed in a beaker of water until the temperature of the liquid is constant. The tube is then tilted, and a piece of filter paper is placed in contact with the point *b* until the liquid in the other limb falls to the mark *a*; the filter paper is withdrawn, and the tube restored to the vertical position. The liquid recedes from the end *b* of the tube and rises in the other limb, and if the temperature becomes higher before weighing, the small bulb offers sufficient space to contain the liquid and thus prevent overflowing.

Various other modifications of the pyknometer have been suggested (Minozzi, Gazz. chim. ital. 1899, 29, i. 406; Leimbach, J. pr. Chem. 1902, 66, 475; Fischer, Chem. Zeit. 1904, 28, 359; Stanford, Phil. Mag. 1905, 10, 269; Bousfield, Chem. Soc. Trans. 1908, 93, 679; Hartley and Barrett, *ibid.* 1911, 99, 1072).

In chemical technology the densities of liquids are most usually determined by means of the hydrometer. This instrument is based on the fact that when a solid floats in a liquid, the weight of the liquid displaced is equal to the weight of the floating body. The general form of the hydrometer is a spherical or cylindrical glass bulb, with a narrow stem, and the bulb is weighted at the bottom so that the instrument floats vertically in the liquid (Fig. 12).

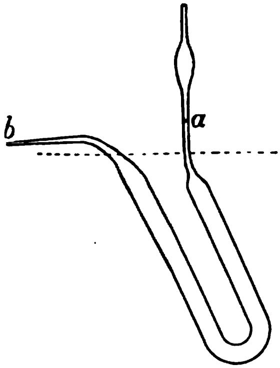


FIG. 11.

FIG. 12.

When the hydrometer is placed in a liquid, it sinks until it has displaced a quantity of liquid equal to the weight of the instrument; it then floats in a position of equilibrium. If placed in a liquid of higher density it will not sink so deep, for the volume of this latter liquid possessing the same weight as the hydrometer will be smaller than in the first case. Again, when placed in a liquid of lower density, it will sink deeper, for a larger volume has to be displaced before the weight of the hydrometer is supported. The density of the liquid is found by readings of the graduations marked on the stem. The stem may be divided to give densities directly, but then the divisions are not of equal length, the differences of length being proportional to the differences of the reciprocals of the densities. Hydrometers, however, are frequently graduated with divisions of equal length, tables being employed to convert the readings into densities if desired. In any case it should be borne in mind that a hydrometer is a comparatively rough apparatus, and too much reliance should not be placed on the readings of any particular instrument, until its scale has been checked at one or two points.

In technical work, hydrometers indicating the specific gravity directly are often used for liquids lighter than water, but almost never in the case of liquids heavier than water. Twaddell's hydrometer, commonly used in this country, is graduated on the same principle as those giving the specific gravity directly, but the readings on the scale are in degrees, each one of which corresponds to a difference of 0·005 in the specific gravity. The zero of the scale is at the point to which the hydrometer sinks in water, so that a reading of 9°Tw., for example, corresponds to a gravity $1{\cdot}000+0{\cdot}005\times9=1{\cdot}045$, and one of 53°Tw. corresponds to the gravity 1·265. To cover the range of specific gravity 1·00–1·85, a set of six instruments is generally supplied. An instrument based on the same principle as Twaddell's hydrometer is the densimeter described by Fleischer (Dingl. poly. J. 1876, 222, 159).

The chief hydrometer with a scale graduated in divisions of equal length is Baumé's, commonly used on the Continent and in the United States. The scale was fixed according to Baumé's original directions in the following manner. For liquids denser than water, 15 parts of pure sodic chloride are dissolved in 85 parts of water at a temperature of 10° Réaumur (12·5°C. or 54·5°F.). The zero of the instrument is the point to which the hydrometer sinks in distilled water, and the point to which it sinks in the 15 p.c. solution of salt is marked 15. The distance between the zero and this point is divided into 15 equal parts, and the whole stem graduated with similar divisions. For liquids lighter than water the zero of the hydrometer is fixed by a 10 p.c. solution of sodic chloride, distilled water giving the division 10. This instrument is, of course, graduated in the opposite direction, the zero being at the bottom of the scale.

Much confusion and irregularity, however, arose in connection with the interpretation of the Baumé degree (*see* Gerlach, Dingl. poly. J. 1870, 198, 315; Chandler, Acad. Nat. Sciences, Philadelphia, 1881). Recently the practice has been to mark the hydrometer 66°B. at the point to which it sinks in 'English sulphuric acid' (93–95 p.c. H_2SO_4) at 17·5°C., and to divide the interval between this and 0° into 66 equal parts. Obviously, this definition of the Baumé degree is not satisfactory, and accordingly attempts have been made to construct a 'rational' Baumé hydrometer. If one of these instruments sinks to 0° in water and to $n°$ in a liquid of specific gravity d, it is easy to show that $\frac{nd}{d-1}=C$, a constant. If now for $d=1{\cdot}842$, n is taken as 66° at 15°C., then C=144·3 and hence $d=\frac{144{\cdot}3}{144{\cdot}3-n}$ (*see* Fuchs, Zeitsch. anal. Chem. 1899, 38, 333). The Baumé hydrometer with a scale based on this formula is commonly used in Germany, but elsewhere other formulæ are employed for the evaluation of the degree. Thus, in Holland, the formula $d=\frac{144}{144-n}$ is taken as the basis of the Baumé scale, in the United States the formula $d=\frac{145}{145-n}$ (*see* Emery, J. Amer. Chem. Soc. 1899, 21, 119). If Gerlach's determination (*l.c.*) of the specific gravity of a 10 p.c. salt solution at 15°C. is taken as a basis, the resulting formula is $d=\frac{146{\cdot}3}{146{\cdot}3-n}$.

In the following table are recorded the specific gravities corresponding to readings of the Baumé instrument, deduced (1) from the formula $d=\frac{144{\cdot}3}{144{\cdot}3-n}$, (2) from the formula $d=\frac{145}{145-n}$.

Degrees n	$d=\frac{144{\cdot}3}{144{\cdot}3-n}$ at 15°C.	$d=\frac{145}{145-n}$ at 60°F.	Degrees n	$d=\frac{144{\cdot}3}{144{\cdot}3-n}$ at 15°C.	$d=\frac{145}{145-n}$ at 60°F.
1	1·007	1·007	34	1·308	1·306
2	1·014	1·014	35	1·320	1·318
3	1·022	1·021	36	1·332	1·330
4	1·029	1·028	37	1·345	1·343
5	1·037	1·036	38	1·357	1·355
6	1·045	1·043	39	1·370	1·368
7	1·052	1·051	40	1·383	1·381
8	1·060	1·058	41	1·397	1·394
9	1·067	1·066	42	1·410	1·408
10	1·075	1·074	43	1·424	1·422
11	1·083	1·082	44	1·438	1·436
12	1·091	1·090	45	1·453	1·450
13	1·100	1·099	46	1·468	1·465
14	1·108	1·107	47	1·483	1·480
15	1·116	1·115	48	1·498	1·495
16	1·125	1·124	49	1·514	1·510
17	1·134	1·133	50	1·530	1·526
18	1·142	1·142	51	1·547	1·543
19	1·152	1·151	52	1·563	1·559
20	1·162	1·160	53	1·580	1·576
21	1·171	1·169	54	1·597	1·593
22	1·180	1·179	55	1·615	1·611
23	1·190	1·189	56	1·634	1·629
24	1·200	1·198	57	1·652	1·648
25	1·210	1·208	58	1·671	1·667
26	1·220	1·219	59	1·691	1·686
27	1·231	1·229	60	1·711	1·706
28	1·241	1·239	61	1·732	1·726
29	1·252	1·250	62	1·753	1·747
30	1·263	1·261	63	1·774	1·768
31	1·274	1·272	64	1·796	1·790
32	1·285	1·283	65	1·819	1·813
33	1·297	1·295	66	1·842	1·835

The Baumé hydrometer for liquids lighter than water is graduated in two ways, the relation between degrees and gravity being given by the formula $d=\frac{146}{136+n}$, or the American formula $d=\frac{140}{130+n}$ (*see* Emery, J. Amer. Chem. Soc. 1899, 21, 119). The following table gives the values of the specific gravity corresponding to the readings of this instrument.

Degrees Baumé	$d=\frac{140}{130+n}$ at 60°F.	$d=\frac{146}{136+n}$ at 12·5°C.	Degrees Baumé	$d=\frac{140}{130+n}$ at 60°F.	$d=\frac{146}{136+n}$ at 12·5°C
10	1·000	1·000	36	0·843	0·849
12	0·986	0·987	38	0·833	0·839
14	0·972	0·973	40	0·824	0·830
16	0·959	0·961	42	0·814	0·820
18	0·946	0·948	44	0·805	0·811
20	0·933	0·936	46	0·796	0·802
22	0·921	0·924	48	0·787	0·794
24	0·909	0·913	50	0·778	0·785
26	0·897	0·901	52	0·769	0·777
28	0·886	0·890	54	0·761	0·768
30	0·875	0·880	56	0·753	0·760
32	0·864	0·869	58	0·745	0·753
34	0·854	0·859	60	0·737	0·745

Other hydrometers designed for liquids lighter than water are occasionally used. In Cartier's hydrometer 21° corresponds with 21°B., but above and below this point 15 degrees Cartier=16 degrees Baumé. In Beck's hydrometer the zero corresponds with $d=1{\cdot}000$ and 30° with $d=0{\cdot}850$: the thirtieth of this interval is 1° and equal divisions are continued in both directions as far as desired.

In addition to the general hydrometers just referred to there are also a number of instruments used for certain special purposes, such as Sikes' hydrometer and Tralles' alcoholometer for ascertaining the strength of spirits (*see* ALCOHOLOMETRY), and various saccharometers for finding the specific gravity of saccharine solutions (*see* SUGAR).

All the foregoing hydrometers are instruments of variable immersion.

Nicholson's hydrometer, on the other hand, is a constant immersion instrument, and consists of a cylindrical metallic bulb connected at the bottom by a wire to a cup, and also an inverted cup pierced with holes. The top of the float is connected by a wire to a pan, on which weights may be placed. This wire has a single mark on it, which is brought to the surface of the liquid by weights placed on the upper scale pan. The instrument is so adjusted that when floating in distilled water at 62°F., 1000 grs. placed on the scale pan will bring the mark on the stem to the surface of the water. When placed in a denser liquid, more weights have to be added to the 1000 grs. in order to bring the mark to the level of the liquid, and as the same volume of liquid is displaced as in the case of the water, the weights at once give the density of the liquid referred to that of water at 62°. The cups below the float are used in the determination of the densities of solids, and will be referred to subsequently.

Another somewhat similar hydrometer consists of a cylindrical glass weight suspended from the arm of a balance, and is so counterpoised that the balance is in equilibrium when the plunger is sunk in distilled water. This is the principle of the Mohr-Westphal balance (Fig. 13). When placed in liquids of other densities the weights have to be altered to bring the balance to equilibrium, and the weights, which are generally used in the form of riders, are so arranged that the density of the liquid is read off directly. A thermometer may be placed within the glass plunger with its bulb projecting below, so that the temperature of the liquid can be determined simultaneously.

Another method of determining the densities of liquids depends on the fact that if columns of two liquids of different densities are made to support one another, the lengths of the columns will be inversely as the densities. An inverted glass U tube with the limbs graduated upwards from 0 near the open ends is employed; at the bend of the tube there is attached a tubulure closed by a stopcock, or by a piece of caoutchouc tube with screw-clip. One of the open ends of the tube is placed in water, and the other into the liquid of which the density is sought, and suction is applied. The liquids rise in the tubes, and after adjusting the outside levels to the zero marks, the lengths of the columns are read off. In order to avoid capillarity effects the tubes should be not less than 6 mm. internal diameter. Various forms of apparatus based on this principle have been described (Hare, Silliman's J. 1826, 11, 133; Alexander, Ann. Chim. Phys. 1847, 70, 137; Tate, Phil. Mag. 1859, 17, 254; Schiff, Annalen, 1862, 121, 82; Weber, Beiblätter, 1879, 3, 770; Girardet, Bull. Soc. chim. 1901, 25, 936; *see* also Watson's Practical Physics, 29; compare Lefebvre, Chem. Zentr. 1897, ii. 402).

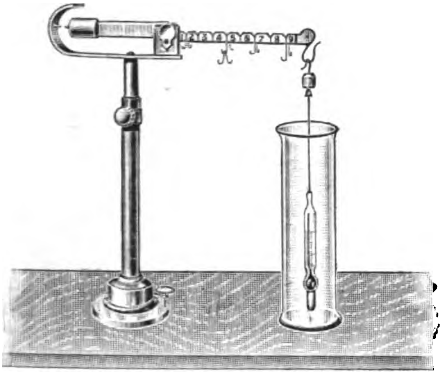


FIG. 13.

For some purposes the density of a liquid has to be determined at its own boiling point. This may be done by suspending a specific gravity flask filled with the liquid in another vessel containing some of the same liquid, which is raised to the boiling point. This heats the contents of the flask, and when the liquid ceases to expand the stopper is placed in the bottle, which is then removed from the vessel, allowed to cool, and weighed (C. Schall, Ber. 1884, 17, 2201). Instead of a specific gravity bottle one may conveniently use a pyknometer of the shape shown in Fig. 14 (Neubeck, Zeitsch. physikal. Chem. 1887, 1, 652). Another instrument employed in finding densities at high temperatures is the dilatometer, which is a kind of thermometer with a graduated tube, the capacity of the tube and bulb being accurately known. The density of the liquid is first determined by the ordinary specific gravity bottle, and then some of the liquid is introduced into the dilatometer, the temperature of which is gradually raised, and the increase of volume measured. When the coefficient of expansion has been thus determined, the density at any temperature may be calculated. For a complete account of the methods of using dilatometers, and all the precautions necessary in their manipulation, *see* Thorpe (Chem. Soc. Trans. 1880, 37, 155; 1893, 63, 262).

FIG. 14.

For the determination of critical densities and of the densities of liquids in contact with saturated vapour at temperatures up to the critical temperature special methods are employed (*see* Ramsay and Young, Phil. Trans. A, 1886, 177, 123; 1887, 178, 57, 313; 1889, 180, 137; Young, Chem. Soc. Trans. 1889, 55, 486; 1891, 59, 37, 125, 911; Proc. Phys. Soc. 1895, 13, 617; Phil. Mag. 1900, 50, 291; Amagat, Compt. rend. 1892, 114, 1093; Young and Thomas, Chem. Soc. Trans. 1893, 63, 1199; Centnerszwer, Zeitsch. physikal. Chem. 1904, 49, 199).

DENSITY OF SOLIDS.

In determining the density of a solid it is necessary to find its mass, and also the mass of an equal volume of water, or, what comes to the same thing, to find the volume of the solid, from which the mass of the water can be calculated. In some few cases this may be done by measurement, as, for example, the measurement of a cubic foot of a body, like stone, which may be cut into a regular shape. It more generally happens, however, that the solid is irregular in shape, or is even in the form of powder: other methods must then be adopted.

One of the simplest methods is to place some water or other liquid of known density in a graduated tube and measure it, and then introduce a weighed quantity of the solid, and observe the rise of level of the liquid in the tube. Or the tube may be weighed before and after the introduction of the solid, the increase of weight giving the quantity of the solid introduced. (Schiff, Annalen, 1858, 107, 59; Osann, Ann. Phys. Chem. 1859, 106, 334; Dobbie and Hutcheson, Phil. Mag. 1884, 17, 459; Erdmenger and Mann, Chem. Zeit. 1893, Suppl. 289; Stanger and Blount, J. Soc. Chem. Ind. 1894, 13, 456; McKenna, J. Amer. Chem. Soc. 1899, 21, 50; Jacobsen, Bull. Soc. chim. Belg. 1904, 18, 198; von Wrochem, Chem. Zentr. 1905, i. 1577). Gentilé (J. Pharm. 1867, [iv.] 5, 401) uses a small bottle with a bulb at the top of 1 c.c. capacity. The bulb is connected to the bottle by a narrow tube with a mark on it, and there is another mark on a similar tube above the bulb. The bottle is filled with liquid to the lower mark and weighed; the solid is introduced until the liquid reaches the upper mark, and the whole is again weighed. This increase of weight is that of 1 c.c. of the solid.

A similar process that may be employed when the solid is in small fragments or in powder is to fill a specific gravity bottle with water, and counterpoise it on a balance. Some of the solid is then placed on the pan of the balance and weighed; the solid is now placed in the specific gravity bottle, and the level of the water adjusted. On again weighing, the quantity will be found to be less than the previous amount, the difference being due to the quantity of water expelled by the introduction of the solid, this water, of course, occupying the same volume as the solid. The relative density of the solid to water at the same temperature is at once found by dividing the weight of the solid by the weight of the quantity of water expelled. Some precautions are necessary in this method. Many solids, especially in the form of powder, entangle a quantity of air, which replaces some of the water in the bottle, or may even cause some of the solid to float in the liquid. This may often be removed by placing the specific gravity bottle containing the water and the solid in an air-pump receiver and exhausting the air; the diminution of pressure causes the entangled air to expand and form large bubbles, which readily escape from the surface of the water.

In the case of solids that are soluble in water this method is obviously inapplicable, and it is necessary to use another liquid of known density which does not act on the solid. Petroleum or alcohol may be used, care being taken to determine the density of the particular sample of liquid used. For a description of the precautions necessary in this method, *see* Tutton, Chem. Soc. Trans. 1894, 65, 650; 1897, 71, 865; Earl of Berkeley, *ibid.* 1907, 91, 56.

When the body of which the density is to be determined is of such a shape that it can be suspended by a piece of fine platinum wire, the piece is first weighed and then attached by means of the fine platinum wire to the hook at the bottom of a small scale pan. A vessel of water is placed under the scale pan, and the solid immersed in it. When a solid is thus immersed in water it displaces its own volume of water, and there is at the same time an apparent loss of weight; this is due to the surrounding water producing a pressure on the solid which is exactly equal to the pressure on the volume of water which the solid has displaced, and which previously kept the water in the vessel in equilibrium. The apparent loss of weight is therefore the weight of the quantity of water displaced by the solid, that is to say of an equal volume of water, so that we obtain the necessary data for determining the relative density of the solid at the temperature of the water at the time of the observation, the mass of the solid divided by the loss of weight in water being the density.

If the body is less dense than water it is obvious that its density cannot be determined precisely in this manner, for the solid will float. To cause it to sink, it is attached to a piece of metal of known weight and density. On weighing the two bodies together in water part of the apparent loss of weight is due to the displacement of the water by the metal and part to the displacement by the light body. The loss caused by the sinker can be calculated from its known weight and density, and this deducted from the total apparent loss of weight gives the weight of the water displaced by the body of which the density is to be determined.

In practice it is, however, better to determine the amount of water displaced by the sinker than to calculate it. The substance may first be weighed, and then the sinker attached by thin platinum wire to the scale-pan and weighed; then a vessel of water placed under the scale-pan, and the sinker immersed in it. The apparent loss will give the quantity of water displaced by the sinker. The substance is now also attached to the wire and weighed, together with the sinker, in water, and the difference between the weight and the sum of the weights of the wire, sinker, and substance is the weight of the water displaced by the sinker and substance. As the weight of water displaced by the sinker has been determined, the difference between these two weights is the amount of water displaced by the substance alone, and the weight of the substance divided by this number gives the density.

The weight of water displaced by the light body may be obtained by the employment of three weighings, whereas the method just described requires four. It depends on the following facts: when a body floats on a liquid it displaces a weight of the liquid equal to its own weight; if the body is now totally immersed there is an upward pressure due to the additional quantity of the liquid displaced; this flotation pressure, determined by weights added to the weight of the body, gives the weight of the liquid displaced by the whole solid. In determining the density of such a body it is therefore necessary to know its weight, the apparent weight of the sinker when immersed, and the apparent loss of weight when the light body is attached to the sinker and weighed under water. The difference between the two last weighings, added to the weight of the body in air, gives the quantity of water displaced by the solid. Thus if P is the weight of the light body, P' the weight of the sinker in water, and P'' the weight of sinker and the light body in water, the density $D=\dfrac{P}{P'-P''+P}$.

Nicholson's hydrometer (as previously mentioned) may be used for the determination of the densities of solids. Weights are placed in the upper scale-pan until the instrument sinks to the mark. The weights are removed, and the substance is placed on the pan, and weights added until the mark is again at the level of the liquid; the difference between the weights is the weight of the solid in air. The solid is then placed on the lower scale-pan if of a higher density than water, or underneath the inverted cup if of a lower density, and weights are placed on the upper scale-pan to restore equilibrium. From the numbers thus obtained the amount of water displaced by the solid can be calculated, and from this, together with the weight of the body in air, the density is determined.

There are some solids which must not be wetted by any liquid, in consequence of a possible change of composition, and in these cases the usual methods of determining densities are of course not available. Others which are porous retain air so persistently that errors may arise by the presence of quantities of air which cannot be removed. In such cases an instrument similar to Say's stereometer (Ann. Chim. Phys. 1797, 23, 1) may be employed. This apparatus is now known as the volumenometer.

The air inclosed in a glass bulb and adjoining tubes is shut off at atmospheric pressure; the space at the disposal of the air is then increased or decreased by a known amount, and the new pressure is read off on a manometer connected with the apparatus. These operations are repeated when the air space contains a known weight of the solid under examination and from the data obtained the density of the solid is calculated. Many forms of apparatus based on this principle have been described (Miller, Phil. Mag. 1834, 5, 203; Kopp, Annalen, 1840, 35, 17; Regnault, Ann. Chim. Phys. 1845, 14, 207; Grassi, J. Pharm. Chim. 1847, 11, 184; Baumhauer, Arch. Néerl. 1868, 385; Rüdorff, Ann. Physik, 1879, 6, 288; Paalzow, *ibid.* 1881, 13, 332; Bremer, Rec. trav. chim. 1898, 17, 263, 405; Mameli and Sanna, Gazz. chim. ital. 1902, 32, ii. 211; Zehnder, Ann. Physik, 1903, 10, 40). A description of one of the more recent modifications (Bremer's) will make clear the manipulation of the volumenometer. The wide-mouthed flask F (Fig. 15), immersed in a small water-bath, is connected through the three-way stopcock R with the tubes *ab* and *cd*, which contain mercury. On *ab* there are two marks or movable rings at *p* and *q*, the volume *v* of the tube between these being accurately known. With the stopcock R turned so as to connect both F and *ab* with the air, the tube *cd* is adjusted until the top of the mercury meniscus is at *p*. The stopcock R is then turned so as to leave F and *ab* in connection but shut off from the air. The tube *cd* is now lowered until the top of the mercury meniscus in *ab* is at *q*, and the difference *h* in level between the mercury in the two tubes is determined with a cathetometer. A similar operation is carried out when the flask F contains a weighed quantity of the solid under examination, the difference in level now found being *h'*. From these data the volume *x* of the solid can be calculated by the formula $x = vH\frac{h'-h}{hh'}$, where H is the barometric height.

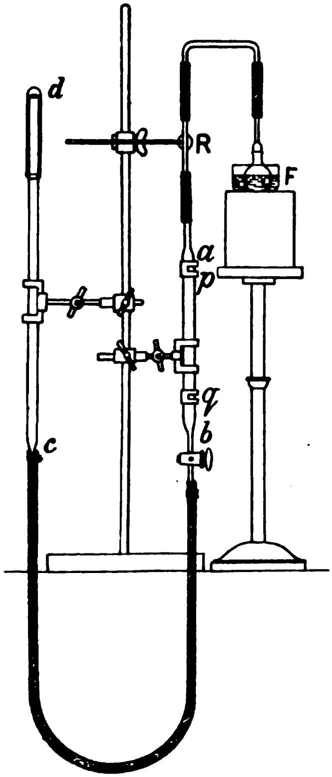


FIG. 15.

The volumenometer obviously cannot be employed for the determination of the densities of solids which give off any gas or vapour under reduced pressure, such as efflorescent salts, for the increase of volume would be due not only to the expansion of the air in the apparatus, but also to the production of aqueous vapour. It answers very well for porous bodies like cotton wool, the entangled air from which at once expands on the pressure being diminished.

Occasionally it is necessary to determine the densities of small fragments of crystals or minerals, and for this purpose liquids in which the solids will just float may be used. The densities of the liquids may be afterwards determined, or a number of solutions of known densities may be kept in readiness. It is obvious that the method is valid only when the solid is not acted on or dissolved by the liquid. For the application of this method *see* Schaffgotsch, Pogg. Ann. 1862, 116, 279; Sonstadt, Chem. News, 1874, 29, 127; Church, Mineral. Mag. 1877, 1, 237; Goldschmidt, Jahrb. Mineral. Beilageband, 1881, 179; Klein, Compt. rend. 1881, 93, 318; Rohrbach, Ann. Physik, 1883, 20, 169; Brauns, Jahrb. Mineral. 1886, ii. 72; Retgers, Zeitsch. physikal. Chem. 1889, 3, 289; 4, 189; 1893, 11, 328; Jahrb. Mineral. 1896, i. 212; ii. 183. Among the heavy liquids used by these authors are a solution of the double iodide of potassium and mercury, which can be obtained of the density 3·196; a solution of cadmium borotungstate (density of saturated solution 3·281); a solution of mercuric and barium iodides, which can be obtained of the density 3·588, but is unstable on mixing with water; and methylene iodide (density 3·33). In the first cases, water is added if a liquid of lower density is required, while benzene is similarly used with methylene iodide. Liquids the density of which is varied in the way described are used not only for determining the density of minerals, but also for separating the constituents of mixed minerals. Fused solids have been employed for a similar purpose (*see*, for example, Thoulet, Compt. rend. 1878, 86, 454; Klein, *l.c.*; Bréon, Compt. rend. 1880, 90, 626).

The floating method of determining the specific gravity of solids has been utilised also in the examination of fats (Hager, Zeitsch. anal. Chem. 1880, 19, 239). In this case the liquid medium is a suitable mixture of water and ethyl alcohol.

It has been suggested (Andreae, Zeitsch. physikal. Chem. 1911, 76, 491) that the foregoing method may be advantageously varied by putting the crystals under examination along with a mixture of methylene iodide and benzene of about the same specific gravity in a dilatometer. This is placed in a bath the temperature of which is slowly altered until the crystals float. From the weight and volume of the dilatometer the density of the liquid can be accurately determined. J. C. P.

SPECTRUM ANALYSIS. I. **Introduction.** When Fraunhofer investigated the solar spectrum he designated the most strongly-marked lines in the visible region by the letters of the alphabet, starting from A at the red end with a wave-length of 7600 ten-millionths of a mm. to K at the violet end with a wave-length of 3930 ten-millionths of a mm. When the extension of the solar spectrum into the ultra-violet region was discovered by photographic methods this lettering of the principal lines was continued into this region as far as the wave-length 2950 ten-millionths of a mm., the letters L to U being used. Owing to the absorption exerted by the great thickness of air through which the light has to pass, the solar spectrum does not extend much beyond the limit of about the wave-length 3000 ten-millionths of a mm.

Recent investigation has shown that oxygen has an absorption band for light of very short wave-length, and that even with an extremely thin layer of oxygen at atmospheric pressure this absorption extends up to at least as far as 1800 ten-millionths of a mm.

It is evident that this absorption sets a lower limit beyond which it is impossible to investigate the ultra-violet spectrum unless a vacuum spectrograph is employed.

Owing to their great convenience as landmarks in the spectrum the Fraunhofer lettering of the principal lines is still used very largely, and in Fig. 1 is shown a diagram in which these principal lines are set out according to their wave-lengths. The elements to which these lines are due are marked at the bottom of the diagram. It may be remarked that A and B are, in reality, absorption lines due to the atmosphere. As regards the extension of the spectrum into the invisible region beyond the red, usually called the infra-red, a considerable portion has been investigated by photographic methods using specially prepared plates. The radiation in this part of the spectrum partakes of the nature of heat, and therefore may readily be investigated by instruments sensitive to heat rays, such as thermopiles, radiometers, radiomicrometers, or bolometers. With these instruments investigations have been pushed to an extraordinary distance, and in one case radiations have been detected in the emission spectrum of a quartz mercury vapour lamp with a wave-length of 3,160,000 ten-millionths of a mm.

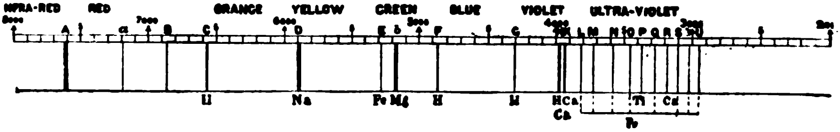


FIG. 1.

Owing to the fact that within the last year or two a new spectroscopic standard has been set up based upon measurements of the wave-length with interference apparatus it will perhaps be advisable to define the various units now used in spectroscopy. The original unit of wave-length used by Ångström himself in his measurements was the ten-millionth of a mm., which is often called the tenth-metre since the unit is 10^{-10} metre. About the year 1890 a new standard of wave-lengths was introduced by Rowland who, basing his measurements upon the well-known coincidence method with gratings, determined the wave-lengths of a very great number of the Fraunhofer lines. From that time until quite recently all spectroscopic measurements were referred to these solar standards of Rowland.

Not long after Rowland published his map, Michelson, by means of interference methods, determined the wave-length of the red cadmium line with exceedingly great accuracy with reference to the standard metre in Paris. Fabry and Perot then, by somewhat similar interference methods, determined the wave-length of a number of iron lines and solar lines in terms of Michelson's value, and showed that there is a periodic error in Rowland's scale.

As the result of Fabry and Perot's work the International Union for Solar Research have decided to adopt as secondary standards of all spectroscopic measurements the means of the values obtained by three independent observers of the wave-lengths of various lines in the spectrum of the iron arc. As all these observations are determined in relation to Michelson's value of the red cadmium line, the International Union have decided that the primary standard for spectroscopic measurements shall be the wave-length of the red line of cadmium $\lambda=6438{\cdot}4722$ Ångströms, and that the Ångström shall be so defined. This unit only differs from the original Ångström unit by less than one part in 10 million. It has also been agreed that all wave-lengths expressed in terms of this standard shall be denoted by the symbol I.A. Since the difference between the new unit and the old Ångström unit is so small it may still be spoken of as the tenth metre, and therefore it may be said that the wave-length of the red cadmium line is $\lambda=6438{\cdot}4722$ Ångströms or 10^{-10} metres, or $643{\cdot}84722\mu\mu$ or $0{\cdot}64384722\mu$. The units μ and $\mu\mu$ are more especially used in cases of the long wave-lengths which, of course, cannot at present be measured with such great accuracy.

It has been further agreed that tertiary standards shall be determined by interpolation between the secondary standards, and this has been done by Kayser for the iron-arc spectrum. These wave-lengths may therefore be used in all cases where great accuracy is required.

II. **The spectroscope.** The limits of absorption exerted by various materials are given below, and from these it may be seen that in spectroscopes, designed for the examination of the visible spectrum, the optical parts may be made of glass, whilst for the examination of the ultra-violet and infra-red rays some other material transparent to one or other of these regions must be substituted.

(*a*) *Direct vision spectroscope.* The simplest form of visual spectroscope is the direct vision instrument in which the dispersion of a very wide-angled dense flint-glass prism is partially corrected by crown-glass prisms. Since in this way it is possible entirely to correct the deviation of the mean rays of the spectrum and only partially correct that of the extreme rays a spectrum will be produced.

The usual arrangement of such an instrument is shown in Fig. 2, where the centre prism p' is made of dense flint glass, and the two outer prisms p, p, of crown glass. In Fig. 3 is shown the complete instrument, which is provided with a slit and eye-piece. This direct-vision spectroscope is very useful for the qualitative investigation of flame spectra or absorption spectra in the visible region, but although in some cases arrangements are made whereby readings of the position of lines or absorption bands can be made upon some form of scale, yet it is clear that such measurements can only be very rough.

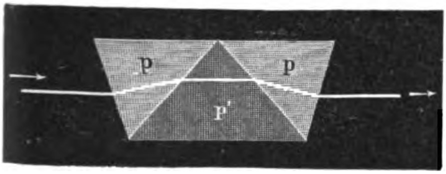


FIG. 2.

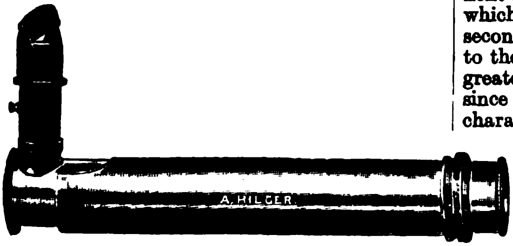


FIG. 3.

(*b*) *Spectrometer.* For more accurate visual work some form of spectrometer must be used, the term spectrometer being applied to a spectroscope in which some device is at hand for the more accurate reading of the deviation of the lines or their actual wave-lengths. In the first case by means of a graduated arc the angular deviation of the lines may be read off, and from these the wave-lengths of the various lines may be obtained, either by the method of graphical interpolation, or by means of a simple interpolation formula as described below. It has been found possible, however, by the use of a constant deviation prism to construct a simple form of spectrometer by means of which the wave-lengths of the lines in the visual region can be read off directly. This instrument is shown in Fig. 4, and is of the fixed arm type, that is the collimator and telescope are rigidly fixed, and the spectrum is made to pass across the field of view of the telescope by rotating the prism. The rotation of the prism is carried out by means of a micrometer screw carrying a drum head, which is so divided that the wave-length of any line under observation may be directly read off. In the best form of the instrument the accuracy of the reading is about 1 Ångström.

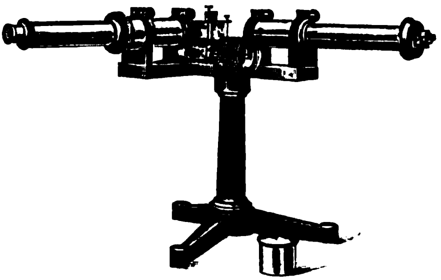


FIG. 4.

(*c*) *The spectrograph.* In accurate work upon the measurement of the wave-lengths of spectrum lines it is necessary to have recourse to photographic methods for two reasons, firstly, a permanent record of the spectrum is thereby obtained which may be measured at leisure; and in the second place, the photographic plate is sensitive to the ultra-violet region, which indeed is of far greater importance than the visible region, since the former generally contains the most characteristic lines of the elements. It is, of course, possible to fit a photographic attachment to either of the spectroscopes mentioned above, yet it is far preferable that the optical parts of the instruments be made of quartz. It would seem from the limits of absorption of the various substances referred to below, that fluorite would even be better than quartz; but unfortunately it is almost impossible at the present time to obtain this material in sufficiently large masses from which to cut prisms and lenses.

The construction of a spectrograph with glass optical parts is simplified by the fact that it is possible to use achromatic lenses which give a flat field upon a photographic plate. It has also been found possible to make achromatic lenses with quartz-calcite or quartz-fluorite combinations. To the first of these there is the objection that calcite exerts an absorption beginning at $\lambda = 2200$A, and to the second there is the objection, already mentioned above, arising from the scarcity of fluorite. It will generally be found, therefore, with a spectrograph the lenses and prisms of which are made of quartz, that the foci of the various spectrum lines lie upon a curve, so that photographic films must be used. Recently, however, there have been introduced spectrographs with quartz prisms and lenses so cut in relation to the optic axes that the whole spectrum from $\lambda = 8000$A to $\lambda = 2000$A may be photographed on a flat plate in good focus.

An essential point is that the photographic plate must be set at an acute angle (27°) with the axis of the telescope lens. An illustration of one of these instruments is shown in Fig. 5.

It is convenient in any spectrograph to have a wooden screen placed in front of the photographic plate, and in this screen to cut a narrow horizontal slot to allow the passage of the spectrum to the photographic plate. The dark slide carrying the plate may then be so mounted as to be capable of movement up and down by means of a rack-work adjustment so that several photographs may be taken upon the same plate.

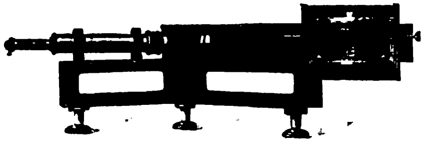


FIG. 5.

Since the determination of wave-lengths in general practice is always carried out by interpolation between lines of known wave-length photographed upon the same plate, it is necessary that the two spectra, the unknown one and the standard, be photographed in juxtaposition. This is most conveniently carried out by the use of draw-slides fitted over the slit, so that any portion of the slit may be exposed at will. The two spectra to be compared are successively photographed through two adjacent portions of the slit, when, of course, it will be found that they are in juxtaposition on the photograph.

It must not be forgotten that, unless precautions are taken, errors may readily be introduced owing to the spherical aberration of the spectrograph lenses. Unless the same portions of the lenses are used in comparing two spectra, it will generally be found that these are not in correct relation to one another upon the photographic plate. If a condensing lens is used to focus an image of the source of light upon the slit, then it is easy enough to obtain photographs of the two spectra in correct relation to one another. The condensing lens is fixed in such a position that its axis passes through the centre of the slit and the centre of the collimating lens, and also at such a distance from the slit that an image of the source may be focussed upon the slit. When the spectra of two sources have to be accurately compared, one of these is placed in such a position that its image is thrown upon a portion of the slit of the spectrograph. A photograph is then taken of the spectrum and, without closing the dark slide carrying the plate, the first source is removed and the second so placed that its image is focussed upon the slit a little above or below the position previously occupied by the first source, and then the second photograph is taken. In carrying out this procedure it will be seen that the draw-slides mentioned above will prove of excellent service.

A very convenient form of spectroscope is one in which a grating is substituted for prisms. A grating may be obtained which has been accurately ruled on a polished surface of glass or speculum metal. The former are used as transmission instruments, whilst in the latter case the spectrum is obtained by reflection.

In a prism spectroscope the dispersion increases with decrease of wave-length, and so the blue and ultra-violet regions appear more extended than the red and orange. In the case of a grating which produces the spectrum by diffraction, as the diffraction is a function of the wave-length, it will be found that the distribution of rays in the spectrum will be much more nearly proportional to their wave-length. Thus, for example, in the visible spectrum it will be found that the yellow rays occupy the middle position. For this reason the dispersion given by a grating is relatively greater in the red and yellow than that given by a prism spectroscope, and hence there is some advantage in using a grating for the study of these regions.

Owing to the difficulty of successfully ruling a grating the cost is necessarily rather high, but it has been found possible to produce excellent replicas at a very reasonable cost. These replicas are produced by making a celluloid cast of a first-class ruled grating. The casts are then mounted upon a flat glass plate, and may be used exactly in the same way as a ruled grating.

III. **Photography of the spectrum.** A few words may be said about the photographic plates to be used in spectrum work. For the blue and ultra-violet regions any good make of plate may be employed, but it is to be remembered that in general better definition is obtained with slow than with rapid plates. If very faint spectra have to be photographed, Wood advises the exposure of the plate for a few moments to a very weak light, such as that obtained from a small gas flame. The actual time for this exposure must be found by trial for the make of plate used, and in one case Wood found that 4 seconds exposure of the plate to the light from a gas flame turned down until the yellow tip is only 3 or 4 mm. high at a distance of 2 metres was necessary. This exposure may be made either before or after the spectrum photograph is taken.

For the red and yellow regions Wratten and Wainwright's allochrome, panchromatic, or spectrum panchromatic plates may be used according to the limits of sensitiveness required. The allochrome plate gives excellent results from the ultra-violet up to the beginning of the yellow. The sensitiveness of the panchromatic plate extends to about $\lambda=7000$, while the spectrum panchromatic extends to about $\lambda=8000$ Ångströms.

If it be required to photograph the regions of greater wave-length than $\lambda=8000$ A, special methods have to be employed for the production of plates sensitive to this region.

Three different methods have been used for this purpose. First Abney prepared special emulsions at a low temperature with which he coated the glass plates. This method has been made more practicable by Ritz. The second method depends on the inverse action of the infra-red rays upon an ordinary photographic plate, which previously has been solarised by exposure for a short time to a weak light. This method has been used by Millochau, who succeeded in obtaining photographic records up to $\lambda=10000$ A. The third method is that known as the phosphorophotographic method, and depends upon the power possessed by infra-red rays of destroying the phosphorescence of zinc sulphide. Bergmann, in using this method, exposed a zinc sulphide screen for 1–2 mins. to an arc light, a second screen of a saturated solution of cupric ammonium sulphate being interposed. The screen is then exposed to the spectrum for 2–8 mins., and then brought into contact with the photographic plate, which after 2 hours is developed. In this way it has been found possible to reach as far as 20000 A.

IV. **Recognition of lines and determination of wave-lengths.** In any work upon qualitative analysis by spectroscopic methods, or in the quantitative estimations described below, it is essential to recognise the lines in any known spectrum, which may most easily be carried out by a determination of their wave-lengths. This is simple enough for the lines in the visible spectrum when a direct reading wave-length spectrometer is used.

In the older form of spectrometer, in which the deviations of the lines are read, or their position on some arbitrary scale noted, it is necessary to reduce the values obtained to wave-lengths. This may be done either by the method of graphical interpolation or by the use of Hartmann's interpolation formula. In the former case the deviations of certain well-known spectrum lines, or their scale readings, are plotted against the wave-lengths on squared paper. When a sufficient number of such points are obtained a curve is drawn through them; the wave-length of an unknown line may at once be read from this curve if its deviation or scale reading is known. For drawing the dispersion curve in the visible region Collie has pointed out that a vacuum tube containing helium, hydrogen, and mercury vapour gives a number of lines eminently suited for the purpose. The wave-lengths and oscillation frequencies of the lines in this spectrum are as follows:—

		Wave-lengths	Oscillation frequencies
Helium	red	7065	14197
Helium	red	6678	14969
Hydrogen	red	6563	15232
Mercury	orange	6152	16250
Helium	yellow	5876	17014
Mercury	yellow	5790	17265
Mercury	yellow	5770	17329
Mercury	green	5461	18307
Helium	green	5016	19932
Helium	green	4922	20311
Hydrogen	blue	4861	20564
Helium	blue	4713	21211
Helium	violet	4472	22357
Mercury	violet	4359	22937
Hydrogen	violet	4341	23031

It will also be found that a vacuum tube containing neon shows a spectrum containing a great number of lines in the red, which are exceedingly convenient for the calibration of the red region.

It will be found that if instead of the wave-lengths the oscillation frequencies of the lines be used, the shape of the curve becomes flatter and easier to draw. By the oscillation frequency is meant the number of wave-lengths contained in 1 cm. *in vacuô*, *i.e.* the reciprocal of the wave-length reduced to vacuum. In order to reduce the wave-length of any line measured in air to its real value *in vacuô*, it is necessary to multiply it by the refractive index of air for the particular wave-length. In making this correction in actual practice it is simplest to add a small number to the wave-lengths. A table of these corrections can be readily constructed, and they lie between 2·5 Ångström at λ=8000, and 0·7 Ångström at λ=2000. Such a table is given complete in Watts' Index of Spectra, App. E, p. 51.

If it be desired to draw the calibration curve from photographic measurements it is simply necessary to measure the distances between the lines on the plate, starting from a chosen line at either end of the spectrum, and plot these against the oscillation frequencies or wave lengths.

As in this case the photographic record will no doubt include the ultra-violet region, the above list of wave-lengths will not, of course, be sufficient. A very convenient set of lines for this purpose is given in the spark spectrum of gold, and the following table contains the wave-lengths and oscillation frequencies of the principal lines of gold and silver, such as are given by gold of ordinary purity. As there are not many strong lines of gold in the red, orange, and green, one or two lines of lithium, sodium, and nitrogen have been included.

No.	Wave-lengths	Oscillation frequencies	Element and intensity
1.	6708·2	16379	Li 10
2.	6457·0	15483	Au 5
3.	6378·4	15927	Au 4
	5896·2	16955	Na 10
	5890·2	16973	Na 10
4.	5837·7	17127	Au 6
5.	5679·8	17601	N 12
6.	5465·5	18291	Ag 10
7.	5230·5	19114	Au 8
8.	5005·7	19978	N 10
	5002·7	19983	N 10
9.	4792·8	20863	Au 8
10.	4488·4	22273	Au 8
11.	4315·4	23167	Au 8
12.	4065·2	24592	Au 15
13.	3898·0	25647	Au 10
14.	3586·7	27873	Au 7
15.	3383·0	29551	Ag 10
16.	3280·7	30472	Ag 10
17.	3122·9	32013	Au 10
18.	3029·3	33001	Au 6
19.	2913·6	34311	Au 9
20.	2825·6	35381	Au 6
21.	2748·3	36375	Au 5
22.	2676·1	37358	Au 12
23.	2641·6	37843	Au 6
24.	2590·2	38595	Au 6
25.	2544·3	39292	Au 5
26.	2503·4	39934	Au 8
27.	2473·9	40409	Ag 8
28.	2447·9	40839	Ag 8
29.	2437·8	41008	Ag 10
30.	2428·1	41172	Au 10
31.	2413·2	41427	Ag 10
32.	2387·9	41865	Au 4
33.	2364·8	42274	Au 10
34.	2352·8	42490	Au 6
35.	2331·3	42881	Ag 8
36.	2304·9	43377	Au 8
37.	2283·4	43781	Au 5
38.	2242·7	44576	Au 5
39.	2229·1	44848	Au 6
40.	2201·4	45408	Au 5
41.	2189·0	45663	Au 5
42.	2166·6	46141	Ag 4
43.	2145·7	46590	Ag 3
44.	2125·3	47038	Au 5
45.	2110·8	47361	Au 6
46.	2082·1	48013	Au 5

For the recognition of the lines in the spectrum and for a measurement of their wave-length Hartmann's interpolation formula will prove of great service. In its original form this formula is as follows:—

$$\lambda=\lambda_0+\frac{c}{(n_0-n)^{\frac{1}{a}}}$$

where λ_0, c, n_0, and a are constants, and n is the linear distance of the line measured from some line chosen as origin. Hartmann showed, however, that since a is nearly $=1$ it may be omitted, which simplifies the formula considerably. As may readily be seen, the values of λ_0, c, and n_0 may be obtained if the wave-lengths and scale readings of three lines in the spectrum be known. It is advisable, of course, that one of these lines be chosen near the middle of the region of the spectrum which is being dealt with, and that of the other two lines, one be chosen at the beginning and the other at the end of the region measured. When the values of the three constants have been found, the wave-lengths of any line can at once be calculated from its scale reading. Although the formula gives more accurate results when short lengths of the spectrum are being dealt with, yet it may be applied over a considerable range with very fair accuracy, and if it only be required to recognise the various lines in a spectrum, the accuracy then given is quite sufficient.

If, however, it is required to measure the wave-length of any new spectrum lines, or if for any other reason greater accuracy is required than can be obtained from Hartmann's formula, the measurement of the wave-length of any line may be found by a simple interpolation between two known lines in the comparison spectrum. Since in a prismatic spectrum the dispersion steadily increases as the shorter wave-lengths are approached, it is advisable in the interpolation to choose two standard lines of known wave-length which are near together, and, of course, one on each side of the line, the wave-length of which is to be measured.

A simple method of approximately determining the wave-lengths of lines from photographs of prismatic spectra has been devised by Edser and Butler. This method consists in photographing a series of interference fringes adjacent to the spectrum to be measured; these interference fringes are produced by Fabry and Perot's method, which consists in causing a beam of white light to pass through a film of air bounded by two parallel sides of half-silvered glass. When this light is examined in a spectroscope, a continuous spectrum is seen, crossed by a series of interference fringes. A sufficiently accurate interference apparatus can be made by taking two pieces of good plate-glass about 3 ins. square, which are each half silvered on one face; the plates are then carefully dried and mounted together, the two silvered faces turned towards one another. The plates are fastened together by a little wax placed all round the edges, when perfect adjustment can be obtained by simply pressing the plates together with the fingers. A preliminary adjustment for parallelism is made as follows: a spot of light or an incandescent electric lamp is viewed through the silvered surfaces; a long train of images due to multiple reflections is generally visible. These images are brought into coincidence, and then, on examining a sodium flame through the apparatus, interference bands will generally be visible. The final adjustment for parallelism is made with the help of these bands, which should be made as broad as possible. In carrying out this adjustment the film is held as close as possible to the eye, because for a parallel air film viewed normally the interference bands are formed at an infinite distance. The perfection of the results finally obtained will depend greatly on the accuracy of this adjustment.

The slit of the spectroscope is illuminated by a slightly convergent beam of light from an arc lamp, and the plates are placed in front of the slit, and as near to it as possible; under these circumstances the spectrum will be found to consist of a series of bright lines separated by black intervals. The best results will be obtained when the plates are in such a position that the slit is parallel to the direction of the interference bands seen with sodium light. The closeness of the bands depends upon the thickness of the film between the silvered surfaces. By means of draw slides, or screens upon the slit, these interference bands are photographed adjacent to the spectrum which is to be measured.

If the interference fringes on a photograph be numbered consecutively, starting from either end, the oscillation frequencies of all the fringes will be in linear proportion to their order number.

The oscillation frequencies of one or two lines at each end of the photograph are plotted against their readings on the interference fringe scale, and a straight line is drawn through the points thus obtained. From this straight line the oscillation frequency of any spectral line can be found at once from its scale reading.

V. **Methods of illumination.** Except in the case of phosphorescent spectra all substances are caused to luminesce when in the state of gas. The following methods of illumination are most usually employed: Flame, electric arc, electric spark, and high potential discharge through gases under reduced pressure.

(*a*) *Flame spectra.* Usually in the case of flame spectra the most convenient flame is that given by the Mecker burner. If it be possible to use an aqueous solution of the salt to be examined, a lasting effect is obtained by the use of the apparatus first designed by Mitscherlich, and which is shown in Fig. 6. The wick at the bottom is composed of fine platinum wires or quartz fibres. A little ammonium acetate added to the solution of the salt is useful in order to make it run well along the wick. In the case of solid substances Hartley recommends as support for the substance thin strips of cyanite or a mixture of carborundum and porcelain clay, which has been fired at a high temperature. It is also convenient in some cases to use a small spoon made of fused silica. Hartley also recommends feeding the burner with gas containing a little chloroform vapour in order to obtain a lasting chloride spectrum.

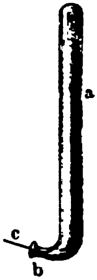


FIG. 6.

Again, a very convenient method of obtaining flame spectra is to introduce into the flame very finely-divided particles of the element itself or of the solution of a salt. In the case of the former, as has been shown by Hemsalech and de Watteville, the air supplied to the burner is passed through a small bulb in which is maintained either a series of electric sparks, or the electric arc between poles of the element to be investigated. In the latter case, the coal-gas supplied to the burner is passed through a flask containing a solution of the salt. This solution is made strongly acid with hydrochloric acid, and a few fragments of zinc are added. The bubbles of hydrogen thereby evolved carry with them into the burner a very fine spray of the solution. An alternative method is to use some form of 'vaporiser' or 'atomiser' by means of which the solution is broken up into very fine spray which is caused to mix with the illuminating gas before it enters the burner.

(*b*) *Arc spectra.* In the case of the electric arc, when the spectra are required of metals which are not easily fusible, the arc may be made between poles of the metal itself or the positive pole (which is the hotter) may be made of carbon. An alternative method is to use a carbon arc and put the substance to be examined in small portions into the crater formed in the positive pole. This, however, has the inconvenience of causing the arc to jump rather badly. A much steadier effect is obtained by using as the positive pole a cored carbon rod in the central hole of which has been packed the substance, the spectrum of which is to be examined. When carbon poles are used for the production of the arc spectra of substances it will, of course, be found that the spectrum shows the lines and bands due to carbon. These may be eliminated by comparing the photographs with one taken of the arc between two pure carbon poles.

(*c*) *Spark spectra.* The third method of illumination is to pass electric sparks from an induction coil or transformer either between electrodes of a metal or between beads of metallic salts which have been melted on to the ends of platinum wires or between an electrode of gold, platinum, or graphite, and the solution of a salt.

In the first case, it is advisable to use a condensed discharge, which may be produced by the introduction of a Leyden jar or plate condenser connected in parallel with the sparking apparatus. It may be pointed out that the most suitable capacity of condenser depends very largely on the size of the induction coil or transformer, and no very definite directions can be given. The condenser should be so chosen that the size of the spark obtained between iron electrodes in air is of the order of 2–3 mm. For the study of the spark spectra of melted salts de Gramont uses two platinum wires, one of which is mounted in a horizontal position, and the other is set above the first, making a somewhat narrow angle with it, so that the two extremities are close together. The two ends of the wires are heated in the Bunsen burner, and a small fragment of the required salt is melted on to the end of the upper wire. The sparks are then passed between the lower wire and the melted bead.

For the study of spectra of solutions a convenient form of apparatus is shown in Fig. 7. In this apparatus the lower platinum wire is surrounded by a narrow, thin glass tube up which the solution ascends by capillary attraction. Another form of sparking apparatus due to Hartley is shown in Fig. 8. In this the electrodes are made of graphite, which is cut into the shape of wedges about ½ in. long and ⅛th in. wide. The wedges are set with their edges parallel to one another, and to the collimating tube of the spectroscope. The wedges are attached to platinum wires and are fixed in glass tubes. The lower wedge dips into the solution, which ascends by capillary attraction up the deep grooves or scratches.

A third apparatus, especially designed for the investigation of quantitative spectra, was used by Hartley and by Pollock, and may be thus described. A piece of glass tube about 6 ins. long and with a capillary bore is bent into the form of a U-tube with the limbs of unequal length, and a small cup, like a thistle funnel, of about 2 c.c. capacity is blown at each end as shown in Fig. 9. A gold wire is then passed through the capillary of the tube so as to project a little above the rim of the lower cup, and a small piece of thin-walled capillary tubing is slipped over the end of the gold wire, and is just so long as to reach the top of the wire and thus draw up the solution and keep the top of the wire well wetted when sparking. It is necessary to employ fairly thick gold wire, and it may be found economical only to use a short piece of gold attached to a thin platinum wire sufficiently long to pass through the capillary. The electrode in the solution must be made the negative, and the upper or positive electrode may be held in any convenient manner, and the spark should not be too long.

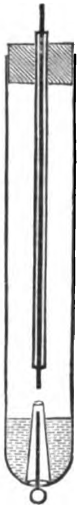


FIG. 7.

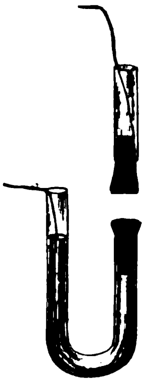


FIG. 8.

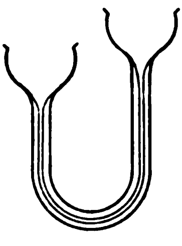


FIG. 9.

Two very convenient pieces of apparatus for obtaining the spark spectra of solutions without the use of metallic electrodes are described by Krulla, the principle being that the spark is made to pass between two jets of the solution. This method eliminates the spectrum lines of the metallic electrodes from the spectrum of the salt.

The phenomena which may be seen in a spark discharge are somewhat complex, for the condensed spark consists of different zones, there being a central part which is very brilliant and is surrounded by an aureole. A spectroscopic examination of the spark shows the rays emitted by the whole spark, aureole, and central portion, and also the rays which are emitted only by the central portion. These two different sets of rays can be recognised as long and short lines in the photograph of the spectrum.

Generally when dealing with spark spectra it is advisable to use a condenser, but in some cases, as will be referred to below, advantageous results are obtained by using the uncondensed spark discharge. It must not be forgotten that in any spark spectra will be found many of the spectrum lines of air. These latter are more pronounced, the less volatile is the substance under examination; for example, the air lines will be found to be very strong in the spectrum of the spark between platinum electrodes. These air lines may readily be eliminated from a spectrum by comparing it with the spectrum of the spark, say between platinum electrodes, when, of course, the lines common to the two spectra will be those due to air. It was shown by Hemsalech that the air lines may be entirely eliminated from any spectrum by introducing self-induction into the secondary circuit. A self-induction coil may be made quite readily by winding wire round a bobbin, the coil so prepared being put in series with the sparking apparatus. The amount of self-induction to be introduced of course varies with the size of the induction coil used. Such a self-induction coil for use with a large Ruhmkorff induction coil is 50 c.c. long, 5 cm. internal diameter, and contains 8 layers of wire each consisting of 150 turns.

(*d*) *Spectra of gases.* The most convenient method for the illumination of gases is to pass the discharge from the induction coil through them under a pressure of from 1 to 3 mm. The gas is enclosed in a vacuum 'tube,' which has two electrodes and a capillary portion, as first designed by Plücker. It will be found that the discharge through the capillary portion of the tube is exceedingly brilliant. If the ultra-violet region of the spectrum is required, either the whole vacuum tube may be made of quartz with no electrodes, or the discharge through the capillary may be viewed end-on through a quartz window.

For the methods employed for making and filling these tubes reference must be made to books on gas manipulation.

(*e*) *Phosphorescent spectra.* An important method of illumination, especially in the study of the rare earths, is that of the cathode streams producing phosphorescence in the substance under examination. It has been found as a result of researches by Crookes, Lecoq de Boisbaudran, Urbain, and others, that very many minerals and artificially-prepared substances give characteristic phosphorescent spectra, but this method of examination finds its chief practical use in connection with the separation of the rare earths from one another.

The rare earth under investigation in the form of oxide or sulphate is placed in a bulb tube provided with two electrodes consisting of flat plates of aluminium, the normals to which lie in the direction of the centre of the heap of material to be examined. Since the cathode rays leave the electrode normal to its surface, it is evident that this construction will give the maximum brilliancy. The exhaustion of the tube is carried to a very high point, the exact degree of exhaustion being judged by the maximum of phosphorescence obtained. For the examination of the spectrum the tube is set at a slight angle, so that the phosphorescent rays can be directed into the spectrograph. When the ultra-violet region is to be examined the phosphorescence tube is provided with a quartz window cemented on and through which the phosphorescent spectrum may be photographed.

VI. Absorption spectra. By an absorption spectrum is meant a continuous spectrum from which certain definite rays, or groups of rays, have been absorbed during the passage of the light through the substance to be examined. It would appear from this that the best source to use for absorption spectrum observations would be one giving a perfectly continuous spectrum. It must be remembered, however, that it is necessary in all quantitative observations of absorption to make accurate measurements of the position of the absorption lines or of the limits of the absorption bands. If, therefore, a continuous spectrum be used it will be necessary that some convenient method of wave-length determination be at hand. Several series of investigations have been carried out in which a source giving a continuous spectrum is used, but it will generally be found that the determination of wave-lengths of the absorption maxima is unsatisfactory and troublesome. By far the best method is to use a source which gives a spectrum consisting of a very great number of lines closely situated together, and not differing very much in their relative intensities. Such a source is a spark between carbon electrodes, which are thoroughly impregnated with the oxides of molybdenum and uranium, as described by Jones. The two carbon rods, about 1 cm. in diameter, are filed to wedge-shaped edges, care being taken that the edge of the wedge is at right angles to the axis of the rod. These carbon wedges are boiled in a solution of uranium nitrate and then dried and heated to dull redness. This process is repeated three times. They are then boiled in a strong solution of ammonium molybdate and again heated to dull redness, this process also being repeated three times. In mounting these electrodes, just as in the case of the spark spectrum described above, the wedges are set parallel to one another, and to the axis of the collimator tube.

The electric spark between cadmium electrodes has been used by Hartley and by Purvis as a source for absorption spectra observations. Although the cadmium spectrum consists of only a few very bright lines, yet the region between these lines is filled with a continuous background which serves extremely well for the observation of fine-line absorption. It must not be forgotten, however, that errors may be introduced if it happens that an absorption band lies very close to the position of one of the bright cadmium lines. For this reason, in dealing with fine-line absorption, it is advisable to use alternately two sources, the cadmium spark and one other, the second one being used merely for the purpose of finding whether any absorption lines are present at or close to the position occupied by the cadmium lines. Hartley has also used the spark between electrodes made of an alloy of cadmium, tin, lead, and bismuth, the metals being melted together in atomic proportions. This, however, does not seem to be so satisfactory as the spark between pure cadmium electrodes.

The use of one of these sources which gives a spectrum of bright lines is manifestly superior to a source giving only a continuous spectrum, because the bright lines, being of known wave-length, serve as land-marks from which the wave-lengths of the absorption lines or bands may be measured.

Owing to the enormous multiplicity of the lines in the uranium and molybdenum coated carbon electrodes mentioned above, some difficulty may be found in recognising these lines and finding their wave-lengths. This spectrum may, however, easily be calibrated by photographing in juxtaposition to it a spectrum containing a few lines of known wave-length, as, for example, the cadmium spectrum. If the photograph then be measured with a travelling micrometer the whole of the molybdenum and uranium spectrum can be calibrated with the help of Hartmann's formula already described. By matching this calibrated spectrum with the photograph of the same spectrum taken when the absorbing substance has been interposed, the limits of the absorption may at once be read off. Very frequently absorption spectrum measurements are expressed in oscillation frequencies and not in wave-lengths.

If it be desired to observe absorption bands or lines in the red and yellow regions of the spectrum, it will generally be found that emission spectra do not contain sufficient lines in these regions to justify their use for this purpose. Some other source must be sought for, and it has been found that very satisfactory results are obtained with interference fringes. These interference fringes are obtained simply enough by the use of the Edser and Butler interference apparatus described above. A source of light giving a continuous spectrum in the red and yellow is used, and by means of a condensing lens a slightly converging beam of light is thrown on to the interference plates, which are placed immediately in front of the slit of the spectroscope. Since the oscillation frequency of the fringes is very easily obtained they may readily be used for the observation of absorption bands.

Although for simple qualitative measurements of absorption in the visible region it may be sufficient to make visual measurements by means of a spectrometer, yet in any accurate work upon absorption it is necessary to determine the position of the maximum of absorption in the case of every absorption band, which is not necessarily its centre; furthermore, it is necessary when possible to determine the limits of concentration over which the absorption band persists. In such accurate work it is obvious that visual work must give place to photographic methods. In order to obtain the position of maximum absorption corresponding to any absorption band the concentration of the absorbing substance is steadily decreased. It will be found that the absorption band or bands become narrower and narrower until they finally vanish. In this way the head of the absorption may be obtained, and this corresponds to the position of maximum absorption in the case of each band. It will be found most convenient to examine the absorption of a compound by dissolving it in some suitable solvent, when the molecular concentration may be decreased simply by lessening the thickness of the solution examined. For this purpose may be used an adjustable absorption cell as shown in Fig. 10, which consists of two glass tubes which fit loosely one inside the other. Both of these tubes are ground flat at one end and square to the axis, and have a quartz plate cemented in each case as shown at A and B. C is a bulb tube sealed to the side of the outer tube, and serves to take up the solution when the thickness of the layer is decreased by pushing in the inner tube. At D a broad india-rubber band is slipped over the junction in order to keep it water-tight, and this may be about 1 in. broad. The outer tube is about 1 in. wide and 6 ins. long, and it has a millimetre scale etched upon it, this scale being so ruled that its zero division coincides with the inner side of the quartz plate A, and thus the reading of the inner side of the plate B upon the scale gives the thickness of the solution. The inner tube is preferably lined with black paper, so as to stop as far as possible the reflection of light from the glass walls. In actual practice a solution of known strength of the substance in a suitable solvent is made of some standard strength, say $\frac{1}{10}$th normal. This is then put into the cell which is adjusted so that the thickness of the layer is 30 mm., and a photograph is then taken of the source after passing through this thickness; the layer is then reduced to 25 mm., and a photograph again taken, this being repeated for the lengths 20, 15, 12, 10, 8, 6, 5, and 4 mm. If, as is most probable, the 4 mm. layer of the solution is not entirely diactinic, the solution is diluted ten times and the spectrum photographed through the same thicknesses as before. If necessary this may also be repeated for solutions of N/1000 and N/10000. Except in certain peculiar cases it will be found that there is no need to dilute beyond N/10000. The photographs thus obtained will give a complete record of the change of absorption to be observed in passing from 30 mm. of N/10 to 4 mm. of N/10000. If it be desired, of course, a normal solution of the substance may also be examined, though this in the case of organic compounds is very rarely necessary. The wave-lengths or oscillation frequencies of the absorption lines, or of the limits of the absorption bands, may be read in the case of these photographs either by comparison with a calibrated photograph of the spectrum of the source or by interpolation between any standard lines in the spectrum. These wave-lengths or oscillation frequencies are plotted against the equivalent concentrations of the substance under examination. Hartley, to whom we are indebted for most valuable work on the absorption of organic compounds, in his earlier papers used the equivalent volume of

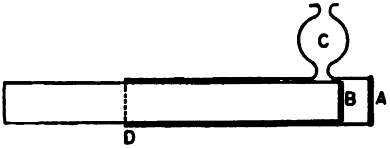


FIG. 10.

solution of a fixed quantity of the substance, and later an equivalent thickness of solution of fixed concentration. In the first case the effect of a given relative change in the amount of the substance was more marked at smaller than at greater concentrations, and in the second case exactly the opposite is true. If, however, the logarithms of the relative thicknesses be used, it will be seen that a given relative change in dilution or thickness will be represented by the same distance on the diagram, whatever be the actual strength of solution. In actual practice the logarithms of the relative thicknesses of the weakest solution used (in the above case N/10000) are put on the ordinates, and the measurements of the absorption limits on the abscissæ, and the line drawn through the points so obtained gives the absorption curve of the substance under examination. Such an absorption curve is shown in Fig. 11, which represents the absorption of acetyl acetone in alcoholic solution.

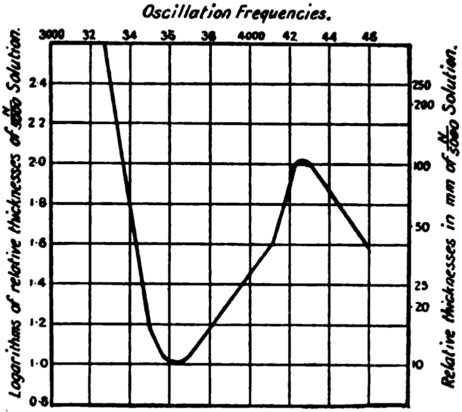


FIG. 11.

As will be shown later, the influence of a solvent upon the absorption exerted by a substance is often very marked, and it may prove of importance to observe the absorption of the substance in the absence of any solvent. This may either be done with the substance in the state of vapour or in the liquid state. Hartley and Purvis have both examined the absorption of the vapours of a number of organic substances, and the method adopted was as follows: A glass tube about 2 cm. wide and 20 cm. long, with quartz plates fastened at each end, is filled with the vapour of the substance by aspirating a current of air previously saturated with the vapour by bubbling it through the substance contained in a small wash bottle.

Since this method does not easily allow the concentration of the substance to be changed, which is necessary in order to obtain the complete absorption curve, a similar tube made of quartz with the ends sealed on may be substituted. To this quartz tube is attached a side tube connected with a small flask containing the substance, and the whole apparatus is exhausted to the highest possible point. The bulb containing the substance is now heated to certain known temperatures at each of which a photograph is taken, this being continued until sufficient concentration is reached. It must be remembered that in order to guard against any condensation of the substance in the quartz absorption tube this must be kept at a constant temperature, which is at least 30° higher than the highest temperature to which the substance is to be heated. The concentration of the substance in the quartz absorption tube may readily be calculated from the vapour pressure curve of the substance under investigation. These observations will give a complete record of the absorption of the substance similar to that obtained for solutions, and from which the absorption curve may be drawn.

For the absorption of pure organic compounds it is evident that very thin layers must be used, and Purvis has devised an apparatus for this purpose, in which a small quantity of the liquid in question is placed between two perfectly parallel quartz plates, and by means of a micrometer screw these plates may be brought closer and closer together, and the thickness of the layer read off at any time. With this apparatus the thickness of the layer may be reduced to 0·003 mm.

VII. **Application of spectroscopic methods to analysis.** Spectroscopic methods have found considerable application in many directions. Although in most cases the use of the spectroscope is restricted to the qualitative analysis of substances, yet it has been found possible to develope certain systems of quantitative analysis by its means. These applications may conveniently be treated under the three headings of emission spectra (flame, arc, and spark), phosphorescence, and absorption.

(*a*) *Emission spectra. Qualitative analysis.* Although in the qualitative spectrum analysis of a substance some knowledge may be gained if the substance give a flame spectrum, yet for complete analysis by the spectroscope recourse must be had to the arc or the spark as a means of illumination, preferably the latter.

In general, owing to its wider application, the spark spectrum is most suited to a qualitative analysis of substances, because they are more often sufficiently good conductors for the high potential current of a spark discharge. Then, again, arc spectra are not possible in the case of solutions. In dealing with solid substances such as, for example, native minerals, it will be found perfectly possible to obtain the spark discharge between fragments of such minerals. These small fragments may be attached by means of fine platinum wire to iron or steel wires, or may be held in small clips which are mounted in any convenient form of sparking apparatus by means of which the spark length can be varied.

In dealing with the spark spectra of solutions it is important that the solution be made the negative pole, and it is most convenient to use an induction coil giving a 2 or 3 in. spark in air. A considerable advantage is often gained by comparing the spectra given by the spark with or without a condenser. When no condenser is used it will be found that the spectrum shows the bands of nitrogen. The solutions of the chlorides of the alkaline earths, metals, and of certain rare earths show with the non-condensed spark, spectra of bands and lines. This is also true for chromium, iron, lead, bismuth, mercury, copper, silver, and gold. The chlorides of the alkalis, tin, antimony, zinc, cadmium, thallium, iridium, gallium, nickel, cobalt, and the platinum family give line spectra. The condensed spark gives almost entirely line spectra, but superposed on these will be the line spectra of air, platinum, and sometimes of chlorine. Considerable differences are often obtained between the spectra given by the spark with or without a condenser, and the unequal sensitiveness of the spectra often affords decided advantages. It is possible for this reason to detect the presence or the absence of various substances in very complex mixtures, which with the condensed spark give such complicated spectra as to make the individual lines very difficult to pick out.

On this account it is sometimes very useful to use a condenser, the capacity of which can be varied at will. Such a condenser can easily be made out of two glass tubes, one of which is sufficiently smaller than the other, so as to slide easily in and out. The larger tube may be about 2 ins. in diameter, and both the tubes are coated on the outside with tin-foil. It is advisable to have a wooden handle fitted to the inner tube, so that it can be moved without danger of touching the coatings with the fingers, and also to have the ends of the wider tube expanded a little, so as to guard against any damage to the inner coating when it is moved in or out.

It has been shown by de Gramont that if the condensed spark discharge be passed between fragments of minerals the spectrum shows bright emission lines, not only of their metallic components, but also of the non-metallic components in a number of cases, as, for example, chlorine, iodine, sulphur, phosphorus, arsenic, and antimony in the case of antimonates and thio-antimonates. In the spark spectrum of no mineral up to the present time have the lines of oxygen and fluorine been noted. We are indebted to de Gramont for an exhaustive study of this method of qualitative analysis of many minerals.

Among the conclusions drawn by de Gramont from his work may be mentioned the following: Those elements which are present only in very small quantities are easily detected. If the condenser is not used the spectra of the non-metals disappear and the metals themselves only show the brightest of the lines. Those minerals which are not good conductors but which are volatile in the spark give equally good results. Fused salts also show the spark spectra both of their metallic and non-metallic elements.

It has been shown by Urbain that minerals such as blende can be analysed spectrographically, using the electric arc. In one case he analysed 64 different samples of blende, and was able to detect quite easily the presence of germanium, gallium, and indium.

It is well known that the arc and spark spectra of the same element frequently differ very considerably. There have been found lines in the latter which are not present in the former. To these Lockyer has given the name of enhanced lines, and has, indeed, suggested that they are due to simpler forms of matter produced under the conditions of great stress existing in the spark. On the other hand, the flame spectrum, as a general rule, is much simpler than that of the arc spectrum, this being attributed to the fact that the temperature of the flame is lower than that of the arc. Again, each particular type of spectrum, whether flame, arc, or spark, is very sensitive to change in the exciting cause, especially is this true in the case of spark spectra, where the relative intensity of the lines is found to change very markedly when the capacity of the condenser or the amount of self-induction in the circuit is varied. It will be evident, therefore, that in such work as quantitative spectrographic analysis great care must be taken to keep the conditions constant throughout the whole series of experiments.

Detection of mercury in explosives. The basis of this method is the electrolysis of a properly prepared solution of the explosive, using a platinum wire as cathode. The platinum wire is then put into a vacuum tube and gently heated, when the mercury may at once be detected by its characteristic spectrum. If the explosive is completely soluble in the ordinary solvents, ether, alcohol, or acetone, 2 grms. of an average sample are dissolved in a suitable solvent and a sufficient quantity of sulphuric or hydrochloric acid is added to give a faintly acid reaction, and the solution is then electrolysed. If the explosive is only partially soluble 2 grms. are first extracted by decantation, the residue is then dried at a low temperature and evaporated with strong nitric acid to destroy all organic matter. It is then taken up with very dilute hydrochloric acid and electrolysed. The solution in the organic solvent is also electrolysed. Since the test for mercury is exceedingly delicate great care must be taken to avoid any contamination during the process of extraction and solution. It is best to use the same dish for solution and for electrolysis.

The electrodes are made of platinum wire 0·015–0·02 in. in diameter and 1 in. long. The dish is nearly filled and is carefully covered with glass or cardboard, the electrodes being passed through this cover. A current of 2 ampères at 10 volts is used, and may be continued all night. The cathode is then taken and carefully dried and dropped into the vacuum tube. This tube is about 2½ ins. long by ⅛th in. in bore. A platinum wire ½ in. long is sealed in at one end, and the other end is drawn out ready for sealing, but leaving sufficient room to allow the entrance of the cathode. The second electrode also is a platinum wire ½ in. long, and sealed in a small side tube. After exhaustion the tube is sealed off and the current from an induction coil passed through it. It is then gently heated, and the presence of mercury is at once recognised by the green line at 5461 Ångström, and also by the two yellow lines at 5790 and 5678 Ångström.

By this method the presence of as little as 0·000001–0·0000001 grm. of mercury may be detected.

The same piece of platinum wire must never be used twice, for it has been found impossible to remove the mercury by the action of heat so that it will not still continue to give the mercury spectrum in a vacuum tube. The amount of mercury present may be estimated quantitatively by placing the cathode in a test tube with a small quantity of iodine and gentl heating it. The mercury is converted into mercury iodide, which then may be treated in any convenient manner.

Quantitative analysis. Hartley has shown, in the first place, that the spark spectra of solutions of metallic salts show the lines of the metallic radicle, and further that the effect of diluting these solutions is first to weaken these lines and then to shorten them until they finally disappear. It has been found on further investigation that all the lines of a metal do not disappear at the same dilution, and further that, given the same conditions, the same lines always disappear at the same dilution. These investigations have been continued by Pollok and Leonard and by de Gramont, and the name of residual or ultimate lines has been given to those lines which persist the longest when the substance is diluted. The method adopted by Pollok, which is based on Hartley's investigations, is to use gold electrodes and to compare the photographs of the spectra given with a 10 p.c., 1 p.c., 0·1 p.c., 0·01 p.c., and 0·001 p.c. solution of a metallic salt. In taking any photograph the spectrum of the spark between the gold electrodes alone is photographed, using a long slit; then the length of the slit is shortened and the spark spectrum of the particular solution required is photographed without moving the photographic plate. In this way the gold lines may at once be recognised. By comparing the photographs taken at various dilutions of the salt the relative persistence of the various rays is obtained. The most persistent, that is to say, the residual lines, have not necessarily any connection with their intensity. It is evident that in the spectroscopic examination for the presence of traces of any element it is by these residual rays that an element may be recognised when present in very small quantities. Inasmuch as it is quite possible, and has indeed been done in very many cases, to determine the dilutions at which the various lines disappear, it may be seen that we have herein a quantitative method of spectrum analysis.

When photographs of the various dilutions of the solution of a particular metal have been taken, the next step is to observe the lines of that metal, which appear at each particular dilution. For the sake of convenience, Hartley indicates the persistence of the various lines by means of the letters of the Greek alphabet in the following way. By ω lines only seen in a 0·001 p.c. solution, by ψ those seen in a 0·01 p.c. solution and not in a 0·001 p.c. solution, by χ those lines seen in a 0·1 p.c. solution but not in a 0·01 p.c. solution, and by φ those seen in a 1 p.c. solution but not in a 0·1 p.c. solution, then by σ those seen in a strong solution and not in a 1 p.c. solution, whilst by τ he denotes those lines which are seen in the metallic spark, but not in any solution.

In actual analysis, therefore, it is only necessary to compare the spectrum photographs taken of the unknown solution with the photographs of the particular metals in the various dilutions, whence the percentage of each particular metal in the substance under examination may be arrived at.

It is hardly necessary to point out that in every photograph the conditions of exposure must be the same, and also in examining the solutions that exactly similar apparatus and electrodes be employed.

The apparatus recommended by Pollok for this particular purpose has already been described in the section dealing with spark spectra. A condenser should be used, and if it be desired to remove the air-lines a self-induction coil may also be inserted.

As a result of the method described above the gold lines may be easily recognised, and the wave-length of the other metallic lines may be obtained by interpolation between the gold lines, using either an interpolation formula or an interpolation curve.

A very large number of these quantitative observations have been made by Pollok and by Leonard on the spectral estimation of the elements, but as yet the investigations are not sufficiently complete to warrant their detailed description as a basis of quantitative spectrographic analysis.

This method can be applied to the quantitative analysis of minerals and alloys; for example, de Gramont has shown that it is possible to estimate by this method the silver in specimens of galena.

Hartley describes the application of this method to the quantitative analysis of alloys; for example, old and rare coins, which, as he points out, saves the cutting and destruction of the coin. He checked his results by making an alloy of the same composition as the coin as found by the spectrographic method, and proved that the spectra of the two were in every way identical. In one case he found 13·96 p.c. of lead, 72·35 p.c. of copper, 12·70 p.c. of zinc, and 0·85 p.c. of iron. He afterwards found that these figures were correct by the ordinary methods of chemical analysis.

Methods have been devised for the quantitative estimation of lithium, sodium, and potassium depending on the persistence of the characteristic lines in the flame spectrum of these elements. For example, Ballman found that if a solution of lithium chloride be diluted until the lithium line ($\lambda = 6708$ Å) disappears, then there is contained in every 3345 c.c. of the solution 0·001 gr. of the lithium salt.

Mottram has devised a method of quantitative estimation of potassium and sodium, which he applies to the analysis of animal tissues and blood. He uses a direct vision spectroscope, with a fixed slit in front of which a piece of cobalt glass is fixed. A Bunsen burner is used, guarded with a blackened metal cylinder having a hole in one side through which the flame is viewed and a slit through which a platinum spoon can be introduced. This Bunsen burner is provided with a platinum gauze nozzle, and in order to keep the gas pressure constant a toluol manometer is used for measuring the pressure and a gas tap with a long arm attached for delicate adjustments. The following precautions were found necessary. The distance at which the spectroscope and cobalt glass is fixed in front of the metal cylinder surrounding the flame must always be the same. The position of the spoon in the flame must be constant, and in Mottram's experiments it was so placed that the bottom of the spoon was just above the apex of the blue inner zone of the flame. The gas pressure was kept very constant as measured by the difference in heights of the toluol columns in the manometer (0·3 cm.). The amount of diffused light in the room must be small and constant. It is best to carry out the experiments in a dark room lighted by an 8 candle-power electric lamp. The spectroscope must always be directed to the same part of the flame; it was directed above the spoon so that the continuous spectrum produced by the incandescent spoon was just invisible. The first definite observations should be postponed until the eyes become accustomed to the dull light of the room (about half an hour). The method for the estimation of sodium depends on the fact that different quantities of sodium sulphate when placed on the spoon and introduced into the flame take different lengths of time to burn off, the time being proportional to the amount. Mottram recommends the use in this case of a second cobalt glass. When the platinum spoon has been cleaned with strong hydrochloric acid and the blowpipe until the D line can no longer be seen through the two cobalt glasses, 0·02 c.c. of the solution under examination containing a known weight of the substance in which it is required to estimate the sodium is placed in the spoon. The D line, which at first is clearly seen, gradually fades until it disappears. The time is then noted, and this time is compared with a table which has been previously prepared when known weights of sodium sulphate were placed on the spoon under identical conditions. From this the percentage of sodium can be estimated.

Mottram gives a table showing the times taken by known quantities of sodium, which vary from 6½ minutes with 0·000001 gr. of sodium to 13 minutes at 0·000003 gr.

The estimation of potassium depends upon the least amount of potassium sulphate that will give the red (potassium line $\lambda=7699{\cdot}3$ Å). In Mottram's apparatus this amount was 0·0000002 gr. Only one cobalt glass was used in this case, and just as before 0·02 c.c. of the solution is placed in the spoon. If the potassium line is then seen, the solution is diluted and again examined, this being continued until the line just becomes invisible. This dilution corresponds, therefore, to 0·0000002 gr. of potassium in 0·02 c.c. of solution.

In the application of this method to the estimation of sodium and potassium in animal tissues and in blood, owing to the fact that carbon and acid radicles other than sulphate materially alter the constancy of the results, great care must be taken in these cases to destroy all carbonaceous matter and to ensure that the sodium or potassium is only present as sulphate.

Phosphorescent spectra. Amongst the many substances which show phosphorescence under the influence of cathode streams perhaps the most interesting are the rare earths. This phenomenon has been frequently used as a means of testing the progress of the fractional separation of the rare earths from one another. Every such method is based on the assumption that the phosphorescent spectrum is a characteristic property of each rare earth. This, however, is not the case, because it has been proved by Leonard and Klatt and by Urbain and his pupils that phosphorescence is a phenomenon characteristic of mixtures of two or more substances. No rare earth gives any phosphorescence when it is pure, and indeed it would seem that no pure substance whatsoever can phosphoresce. Urbain has shown that phosphorescence is a property of diluted matter, and that in order to obtain the phosphorescence of a substance it is necessary that it be mixed with a large quantity of some diluent. To the active principle of such mixtures has been given the name of phosphorogene, and for every pair of substances, phosphorogene and diluent, there is one definite mixture which gives an optimum of phosphorescence. On either side of this optimum, that is if the phosphorogene be either increased or decreased, the phosphorescence is weakened. Moreover, a phosphorescent spectrum as a rule contains several bands, and there is an optimum condition for each of these bands; also these conditions are not the same for all the bands in any one spectrum. It may happen that as the quantity of phosphorogene is increased in a given mixture the conditions are successively arrived at for giving the optimum for each of the bands in turn, with the result that the colour of the phosphorescence appears to the eye materially to alter. Generally speaking, the optimum condition corresponds to the presence of a very small quantity of the phosphorogene. It will be understood from this that the variations in the phosphorescence observed during the fractional separation of the rare earths, will be very varied as the optimum condition for each of the phosphorogenes present is passed. The extraordinary variations which can be obtained in the relative intensity of the various bands in any one phosphorescent spectrum explain why it has been thought by some people that each separate band is the characteristic spectrum of a single element.

Urbain's investigations have proved conclusively that this theory is completely untenable, and they also show the great care that must be exercised in the interpretation of any phosphorescent spectrum that is observed. At the same time, in the fractional separation of the rare earths, owing to the very small differences in their atomic weights, it is necessary to use some physico-chemical observations (such as spectroscopic) to characterise the elements.

In this connection may be used emission, absorption, and phosphorescent spectra, all three of which are given by the rare earths.

In carrying out any fractional separation on the rare earths, if the order number of the fraction is made the abscissa and the atomic weight the ordinate, the curve drawn through these points at the beginning of the fractionation will of course appear continuous and regular. As the fractionation advances the curves will begin to give indications of horizontal steps, which become more marked as the process is continued. These steps, as a rule, correspond to the existence of pure substances. They may, however, be mixtures similar to constant boiling mixtures in a distillation. It is evident from what has been said above, if these horizontal steps give any evidence of phosphorescence that they must correspond to a mixture, and that if they correspond to single pure substances they will not phosphoresce.

It will be seen, therefore, that although phosphorescence cannot be utilised as a test for the purity of a substance, yet it may within certain limits be of great value for the characterisation of an element. But for the complete identification of such an element it is necessary also to make use of its emission and absorption spectra.

Absorption spectra. Perhaps it may not be out of place before dealing with specific absorption spectra observations to define the limits of transmission of the various materials which are used in different branches of spectroscopy.

Substance	Transmits all rays between		
Heavy flint glass	2μ	and	0·3500μ
Flint glass	2μ	and	0·3300μ
Crown glass	2μ	and	0·3200μ
Light crown glass	2μ	and	0·3000μ
Quartz	4μ	and	0·2000μ
Calcite	2·2μ	and	0·2150μ
Fluorite	7·6μ	and	0·1230μ
Rock salt	18μ	and	0·2000μ

Frequently in constructing spectroscopes it is necessary to make use of a reflecting mirror of some kind. It may be pointed out that a silvered surface has very poor reflecting power in the ultra-violet region. The maximum of transmission by a silver layer lies between 3360 and 3100 Ångströms, and such a layer consequently cannot reflect light of this wave-length. A speculum metal surface, however, seems to have the power of reflecting ultra-violet light down to the shortest wave-length yet observed. Similarly a nickelled surface has excellent reflecting power in the ultra-violet region. Nickelled mirrors may easily be obtained by exposing the surface to be coated to the cathode streams from a nickel cathode in a high vacuum.

Absorption spectra of inorganic salts and their lakes with alkannin. Many metallic salts which give coloured solutions may be recognised by their absorption spectra. Those, however, which give colourless or only weakly-coloured solutions, with the exception of praseodymium, neodymium, erbium, samarium, holmium, thulium, europium, gadolinium, and dysprosium do not give sufficiently characteristic absorption for their recognition. It is possible, however, in many cases to convert these substances into compounds which give a characteristic absorption spectra, for example, manganese salts, which although rose coloured, give no characteristic absorption, but if they are converted into permanganates by oxidation with nitric acid and lead peroxide the absorption spectrum becomes highly characteristic. Similarly aqueous solutions of cobalt salts though red possess no characteristic absorption, but their solutions in the presence of concentrated hydrochloric acid give again a highly characteristic absorption.

Formánek has made a careful investigation into the absorption spectra of the lakes formed by metallic salts with the dye-stuff alkannin, which may be used in the qualitative testing for the presence of the metals. It is necessary to use a rather dilute solution of the alkannin in alcohol. The powdered alkanna root is extracted in the cold with 95 p.c. alcohol until a layer of the solution 10–12 mm. thick shows all the absorption bands sharply separated. About 5 c.c. of this solution are then put into a cell about 10–12 mm. thick and two or three drops of the neutral aqueous solution of the metallic salt are added. If after a short time no change in the spectrum is noticed a small drop of dilute ammonia is carefully added and the absorption spectrum observed. The salt solution must be perfectly neutral, and in case of the heavy metals great care must be taken in adding the ammonia to guard against any insoluble precipitate being formed. The solution of the alkannin in alcohol shows four absorption bands at the following wave-lengths 5637, 5443, 5227, and 4872 Ångströms. The addition of dilute ammonia to this solution changes it from red to blue, and it then shows only two bands at λλ=6428 and 5948. If the chloride of the metal is added to the neutral alcoholic solution of the dye-stuff the absorption changes in the case of the following metals, iron, aluminium, glucinum, yttrium, erbium, zirconium, thorium, vanadium, indium, molybdenum, nickel, copper, palladium, rhodium, and uranium. In the remaining metals no change is observed until after the addition of ammonia. In the table on p. 127 are given the maxima of the absorption bands obtained with the various metals.

Absorption of the oxides of nitrogen and ozone in the infra-red and their quantitative estimation. Warburg and Leithäuser have measured the absorption of N_2O_5, NO_2, N_2O_4, NO, N_2O, and O_3 in the infra-red, and find that all these gases exhibit very well marked and characteristic absorption bands between the limits 2·7 and 7μ.

The apparatus used was a fixed arm spectrometer with a single fluorite prism. The source of illumination was a Nernst lamp, and the absorption bands were detected by means of a vacuum bolometer, whilst the wave-lengths of the absorption bands were calculated from the known dispersion curve of fluorite.

In the following table are given the wave-lengths of the absorption bands, in each case the most important band being marked in heavy figures :—

Substance	Absorption maxima in μ						
N_2O_5	2·73	2·83	3·33	3·86	4·27	4·81	**5·81**
N_2O_4	5·695						
NO_2	3·38	**6·11**					
NO	5·24	5·40					
N_2O	2·79	3·54	3·86	4·02	(4·29)	**4·45**	
O_3	4·74						

The absorption of these gases can be utilised for the quantitative analysis of the gas mixtures which contain one or more of these gases, provided that their quantities are not too great. A 30-cm. long absorption tube is used, and it is necessary to determine the intensity of the absorption band in each case corresponding to definite percentages of the gas in question. These percentages should be so small that the partial pressure of the gas lies between 0·3 and 1 mm. When these relations between intensity, and absorption and partial pressure of the absorbing substance have been determined for all the above gases the estimation of the amounts present in any given gas mixtures may readily be found.

Element	Principal band	Secondary Bands		Remarks
Uranium	6870	6315	—	Without NH_3
Iron	6545	6030	—	Ferric chloride with NH_3
”	5895	5475	—	Ferrous chloride with NH_3
Palladium	6418	5875	5447	Without NH_3
”	6084	5629	5234	With NH_3
Caesium	6410	5922	—	With NH_3
Rubidium	6397	5914	—	With NH_3
Potassium	6387	5910	—	With NH_3. Nitrate gives the same spectrum
Cobalt	6370	5845	5405	Chloride with NH_3
”	6354	5832	5395	Nitrate with NH_3
Sodium	6337	5857	—	With NH_3. Nitrate gives the same spectrum
Thallium	6288	5770	—	With NH_3
Barium	6281	5805	5395	With NH_3
Titanium	6271	5782	5350	With NH_3
Strontium	6223	5757	5348	With NH_3
Lithium	6210	5745	5340	With NH_3
Nickel	6192	5725	5320	Without NH_3
”	6198	5732	5325	With NH_3
Manganese	6171	5707	5303	With NH_3
Calcium	6147	5682	5276	With NH_3
Lanthanum	6120	5662	5262	With NH_3. Nitrate gives the same spectrum
Cerium	6115	5658	5258	Chloride with NH_3
”	6123	5665	5265	Nitrate with NH_3
Vanadium	6099	5643	5250	Without NH_3
Praseodymium	6090	5636	5240	Chloride with NH_3
”	6117	5660	5260	Nitrate with NH_3
Magnesium	6064	5614	5213	With NH_3. Nitrate gives same spectrum
Neodymium	6058	5603	5222	With NH_3
”	6055	5601	5220	Nitrate with NH_3
Thorium	6081–6055	5614–5599	5213–5195	Chloride without NH_3
”	6084–6066	5625–5614	5222–5213	Nitrate without NH_3
Zirconium	6030–6016	5581–5570	5195–5186	Without NH_3
”	6058–6030	5603–5581	5213–5195	Nitrate without NH_3
Yttrium	6021	5581	5195	Without NH_3
”	6016	5570	5177	With NH_3. Nitrate gives the same spectrum
Zinc	6016	5581	5195	With NH_3
Erbium	6010	5559	5177	Without NH_3
Indium	5961	5537	5168	Without NH_3
Copper	5953	5515	5128	Chloride without NH_3
”	5945	5509	5123	Nitrate without NH_3
Aluminium	5857	5425	5048	Without NH_3. Nitrate gives the same spectrum
Molybdenum	5845	5415	5040	Without NH_3
Glucinum	5820	5385	5008	Without NH_3

In making use of this method of investigation it is not advisable to use the metallic salts in too dilute a solution.

Absorption spectra of nitrogen peroxide in the visible region and its estimation thereby. Nitrogen peroxide, as is well known, exhibits a very characteristic absorption spectrum, which consists of a large number of fine lines in the visible region and a general absorption in the violet. Robertson and Napper have utilised this absorption for the quantitative estimation of small quantities of nitrogen peroxide in air or carbon dioxide. The absorption spectrum was photographed in each case with a spectrograph having a single dense flint glass prism. A Welsbach incandescent mantle was used as a source of light, and the absorption vessel was a glass tube 40 cm. long with the ends closed by glass discs which were attached by cement. The estimation of the nitrogen peroxide in any gas is done by comparison of the photographs taken of the absorption exerted by the gas, with a series of photographs of the absorption spectra of carbon dioxide or air containing known definite amounts of nitrogen peroxide. It was found possible to estimate quantitatively an amount of nitrogen peroxide as low as 0·05 p.c. within 0·02 p.c. In the case of greater concentrations of nitrogen peroxide the accuracy is about 0·05 p.c.

Quantitative estimation of the nitrogen evolved in the decomposition of gun-cotton and nitroglycerin. The above described method for the estimation of nitrogen peroxide has been applied to the Will test of decomposing gun-cotton and nitroglycerin.

The most satisfactory results in the case of gun-cotton, and also of nitroglycerin, were obtained by heating the substance in a measured current of pure carbon dioxide, and passing the gases through an absorption spectrum vessel as described above, and afterwards through a tube containing copper heated to redness. The gases from this decomposition tube were passed into potassium hydroxide solution and the total nitrogen measured. In the case of gun-cotton 2½ grms. are heated in an oil-bath to 135°, and a stream of specially pure carbon dioxide is passed at the rate of 1 litre per hour (controlled by observing the number of bubbles per minute in a small glass washing bottle containing sulphuric acid) through the vessel containing the nitrocellulose. The current of carbon dioxide containing the gases resulting from the decomposition of the nitro-cellulose is passed through the absorption spectrum tube and the spectrum photographed at intervals of a quarter of an hour. The gases are then passed through a combustion tube containing two spirals of reduced copper gauze and layers of Kreusler's copper oxide asbestos and reduced copper asbestos. The oxides of nitrogen are thereby reduced to nitrogen and the organic gases oxidised to carbon dioxide. The gas is then passed through a measuring burette containing strong caustic potash, and the volume of nitrogen is read at intervals. A curve is constructed showing the amount of nitrogen peroxide and of nitrogen evolved each quarter of an hour, and the character and slope of the curve is a measure of the stability of the sample.

Since certain preliminary experiments proved that water vapour has no influence upon the absorption spectrum of nitrogen peroxide, whilst the presence of liquid water causes a rapid absorption of this gas, great care must be taken not to allow any water to condense in the apparatus. It was found that about 40 p.c. of the nitrogen evolved by the gun-cotton is in the form of nitrogen peroxide.

In the case of nitroglycerin, Jena glass wool soaked in 0·3–0·5 grm. of nitroglycerin is placed in a horse-shoe shaped tube; this is closed by a stopper, which is greased and mercury-sealed. To each end of the horse-shoe is connected a spiral tube s_1 and s_2 in Fig. 12. The current of carbon dioxide may be passed down the right-hand spiral through the glass wool and up the other spiral or *vice versâ*, according to the way the three-way cocks are turned. The whole apparatus can be rotated round the axis, and, when starting, the spiral s_1 is immersed in an oil-bath of known temperature, and so the carbon dioxide receives a previous heating before it reaches the nitroglycerin. Spiral s_2 is protected by an asbestos sheet from the heat of the oil-bath, and is cooled by an air blast. Any volatilised nitroglycerin is condensed in this spiral. After a reasonable time has elapsed the apparatus is rotated through 180°. The two spirals now exchange their functions, and any nitroglycerin in s_1 is restored to the system. The gases are then passed, as described above, first through the absorption spectrum tube and then through the heated tube of copper and copper oxide. In order to guard against any presence of nitroglycerin in the gases they are made to pass through a worm cooled with ice immediately on leaving the decomposition apparatus. As in the case of gun-cotton, described above, the current of carbon dioxide passes at a measured rate and the nitrogen peroxide is spectroscopically estimated by the method described for that substance.

The decomposition of nitroglycerin was studied between the temperatures of 90° and 135°, and it was found that this decomposition proceeds in as uniform a manner as that of a stable gun-cotton. Further, the whole of the nitrogen is evolved as nitrogen peroxide. Between 95° and 125° the rate of decomposition is a function of the temperature, and is doubled for every increase of 5°.

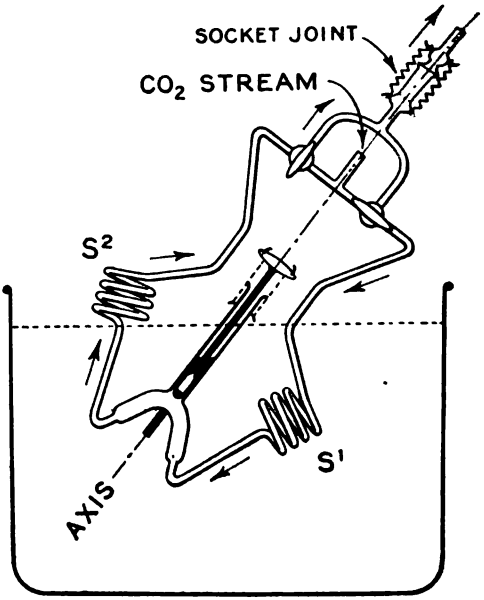


Fig. 12.

VIII. **Spectrophotometry.** In dealing with the quantitative analysis of substances which exhibit absorption two general methods may be employed. Firstly, the amount of an absorbing substance present in any given mixture may be determined by taking a photograph of the absorption exerted by the mixture, and comparing this with a series of standard photographs which have been taken of the absorption of the same substance at certain definite and known concentrations. That standard which exactly matches the absorption given by the unknown mixture will, of course, give the concentration of the absorbing substance in that mixture.

An example of this method has already been given above in connection with the estimation of nitrogen peroxide in the gases evolved on heating gun-cotton and nitroglycerin. It is manifest that exactly the same principle may be applied to substances in solution, provided that standard absorption records can be obtained of known concentrations of the same substance in the same solvent.

In the second method the amount of absorption exerted by the substance in a given mixture is determined quantitatively by means of a spectrophotometer, these observations being made at that region of the spectrum where the characteristic absorption by the substance occurs.

Before giving an account of the instruments and methods employed, a few words may be said about the laws of absorption and their application to quantitative analysis.

If light of intensity I enters an absorbent medium having a thickness equal to 1, the light which emerges will be reduced to $1/n$, and after passing through a second layer of equal thickness the intensity will be reduced to $1/n^2$. If the thickness of the layer be denoted by d, the intensity of the light will be reduced to $1/n^d$. From this it may be seen that as the thickness of the layer increases in arithmetical progression, the transmitted light will decrease in geometrical progression.

If, therefore, the intensity of the incident light be put equal to I and dI be the amount lost during its passage through a layer of thickness dx, we have $dI = -kIdx$.

If we integrate between the limits $x=0$, when the intensity of the incident light $= I_0$ and $x=d$, when the intensity is I, then it will follow that

$$I = I_0 e^{-kd} \quad . \quad . \quad . \quad . \quad (1)$$

where k is a constant depending on the absorbing medium and the wave-length of the light, and e is the base of natural logarithms.

Usually e^{-k} is denoted by the symbol a, and is known as the absorption coefficient, so that we may write

$$I = I_0 a^d \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and if $d=1$, we have $a = I/I_0$, so that a represents the fraction of the light which is transmitted by a layer of thickness I. This relation is known as Lambert's law. Bunsen and Roscoe expressed the absorption power of a given region of the spectrum in terms of the 'coefficient of extinction,' and defined this as the reciprocal of that thickness which causes the reduction in intensity of the light to $\frac{1}{10}$th of its original value. If this coefficient of extinction be expressed by α then, when in equation (2) $I/I_0 = \frac{1}{10}$, $d = \alpha$, therefore $a^{\alpha} = \frac{1}{10}$, whence $a = 10^{-\alpha}$.

Substituting this in the general equation (1) we have $I = I_0 10^{-\alpha d}$, and if I_0 be put equal to 1 then $-\log I = \alpha d$.

In actual practice it is simpler to use a layer of unit thickness ($d = 1$ cm.) when the coefficient of extinction can at once be obtained. For example, let us suppose that a beam of light is reduced to $\frac{2}{5}$ths of its intensity when transmitted through 1 cm. of an absorbing solution.

From this it follows that —

$$\alpha = -(\log \tfrac{2}{5}) = \log 5 - \log 2$$
$$\alpha = 0{\cdot}69897 - 0{\cdot}30103$$
$$\alpha = 0{\cdot}39794.$$

The determination of the extinction coefficient is therefore exceedingly simple.

In order to apply this to the quantitative estimation of absorbing substances we make use of the relation known as Vierordt's absorption ratio. According to Beer's law the absorption of a given solution is inversely proportional to the concentration, that is, if the absorption were observed of a given thickness of a solution of concentration c, the same absorption would be exhibited by half that thickness of a solution of concentration $2c$.

It follows, therefore, that in solutions of different strengths of the same substance the extinction coefficient is proportional to the concentration c.

If the concentrations of a series of solutions of the same substance be expressed by c, c_1, c_2, . . . and the corresponding coefficient of extinction by α, α_1, α_2, . . ., then it follows that $\frac{c}{\alpha} = \frac{c_1}{\alpha_1} = \frac{c_2}{\alpha_2} = A$. From this we have generally $c = \alpha A$, when A is called the absorption ratio. A may be determined once for all for any substance in the given solvent, and the concentration of a solution of the same substance in that solvent may at once be determined by finding the extinction coefficient and substituting it in the formula $c = \alpha A$.

It must be remembered, of course, that the above relation is only true for any one wave-length.

It is evident also that the above relation only holds good when a single absorbing substance is examined in a non-absorbing solvent, and that if two absorbing substances are present, such as occur when the solvent exerts absorption, or when two absorbing substances are dissolved in a diactinic solvent, the observations become a little more complicated. It is necessary in such a case to determine the extinction coefficient for light of two different wave-lengths. If, for example, we have a solution of two coloured substances of unknown concentration, x and y respectively, it is necessary to determine the extinction coefficient for two different parts of the spectrum. Let these be α and α_1 respectively. Then if A and A_1 and B and B_1 be the absorption ratios for the two substances at the two different wave-lengths, it follows that $\alpha = \frac{x}{A} + \frac{y}{B}$ and $\alpha_1 = \frac{x}{A_1} + \frac{y}{B_1}$.

Solving these two simultaneous equations we get $x = \frac{AA_1(\alpha B - \alpha_1 B_1)}{A_1 B - AB_1}$ and $y = \frac{BB_1(\alpha A - \alpha_1 A_1)}{AB_1 - A_1 B}$ from which, of course, the concentrations of the two substances may at once be calculated.

The measurements of the amount of light absorbed by or transmitted through substances such as are required for the determination of the extinction coefficient are made with a spectro-photometer, which is an instrument by means of which the relative intensities of two different beams of light may be compared at any required wave-length in the visible spectrum.

The Vierordt instrument consists in the main of an ordinary spectrometer, the slit of which is divided into two, an upper and lower portion, which are provided with separate micrometer screws for adjusting the width. If both halves of the slit are set at equal width, and are illuminated with a beam of white light, and in front of one half is placed the absorbing material, there will be seen in the eye-piece two spectra, one above the other, one of which is less intense owing to the absorption which has taken place. The difference in intensity between the two spectra at any given wave-length may be determined at once by decreasing the width of the half of the slit corresponding to the brighter spectrum until the two appear equal in the field of view of the telescope. If the original widths of the slit were, say 100, and the one half had to be reduced to 75 in order to establish equality, then clearly the relative intensities were as 4 : 3.

In order to guard against the eye being confused by the intensities of the spectral regions on either side of the region dealt with, the eye-piece is provided with adjustable screens in order to shut off all the rays except those actually to be compared.

There are, however, several points of importance which must be attended to in order to make accurate measurements, and these necessitate the apparatus being more complex than the above simple description would foreshadow. In the first place, the original idea of Vierordt depends upon the assumption that the intensity of illumination is directly proportional to the width of the slit. This cannot be true with a slit of the ordinary type in which only one jaw is movable, so that the slit widens unsymmetrically. This difficulty was surmounted by Krüss who substituted for the Vierordt double slit one in which both jaws of each slit are equally moved in opposite directions by the micrometer screws. Each slit of the instrument is, therefore, opened or closed symmetrically. Again, the intensity of illumination is only proportional to the slit-width when the latter is small. If, therefore, the difference in intensity between the two spectra is very large, it is not possible to measure this only by altering the slit-widths. The intensity of the brighter spectrum is first reduced by introducing a plate of neutral tinted glass, and the final adjustment made by altering the width of the slit. Several of these plates of tinted glass should be on hand, the absorption of which for the various spectral regions has been carefully determined.

In the second place it must be remembered that the loss of light suffered when a beam of light passes through an absorbing layer is not only that due to the absorption of the medium, but that a very appreciable amount is lost by reflection at the boundary surfaces. For example, if an absorption cell half full of the absorbing solution were placed in front of the slits of the Vierordt instrument so that the lower slit was illuminated by the light after passage through the absorbing layer while the upper slit received the light which passed through the upper and empty half of the cell, then the differences observed between the two spectra would not be that due to the absorption alone. The loss by reflection of the light would not be the same in the two cases, for, on the one hand, the reflection would be at a glass-solution surface, and in the other case it would be at a glass-air surface. As the indices of refraction for air and the solution are different the amount of loss by reflection would also differ. This difficulty may be removed by means of what is known as the Schultz corrector. This is a block of glass of the same quality as that of the walls of the cell and is shown at A in Fig. 13.

The internal thickness of the cell is made 11 mm., and that of the Schultz corrector 10 mm., and the depth of the latter is half that of the cell. The cell is filled with the absorbing solution and is set up in front of the slits of the instrument so that one slit receives the beam after passage through 1 mm. thickness of solution, and the other slit receives the beam after passage through 11 mm. If the cell and corrector are made of the whitest flint glass no appreciable absorption is introduced by the latter except in the extreme violet, whilst the difference in loss by reflection is reduced to a minimum.

The third point, and the most difficult of realisation, is the necessity that the two spectra should be in optical contact in the field of view. The eye is exceedingly sensitive to differences in intensity between two spectral images, provided that there is no sharply defined line of separation between them. It may be readily understood that however carefully the above cell be adjusted in front of the Vierordt slits, it will practically be impossible to obtain the two spectra in contact without a dividing line. In order to bring the two spectra into contact H. and G. Krüss applied the so-called Hüfner rhomb to the Vierordt instrument, the arrangement being shown in Fig. 14.

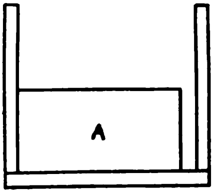


FIG. 13.

The two beams coming from the absorbing cell with the Schultz corrector enter the rhomb. and emerging thence they enter the slit and give two spectra in contact.

In the Vierordt instrument the intensity of the spectra is altered by varying the width of the slit, the assumption being made that the intensity is proportional to the slit-width, provided that this latter is kept small. Many forms of spectrophotometer have been devised from time to time, and a different method of altering the intensity adopted. In the Glan type the two beams are polarised at right angles to one another by suitable means, and they finally pass through a Nicol prism. A rotation of this will, therefore, decrease the intensity of one and increase the intensity of the other, and the relative intensities of the two may be calculated from the angle θ through which the Nicol is rotated, for $\frac{I}{I_0} = \tan^2 \theta$. In the Hüfner instrument only one beam is polarised, and the change in intensity is altered by the rotation of a Nicol prism as in the Glan instrument. In the older forms of the Hüfner instrument the brighter beam, that is to say, that light which has passed through the thinner layer of absorbing solution was polarised by reflection from two plane mirrors set at the polarising angle outside the slit. In

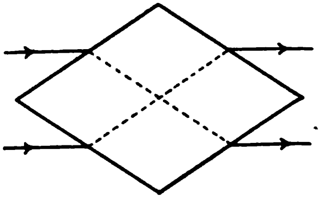


FIG. 14.

the modern form the beam of light after transmission through the thinner absorbing layer is passed through a Nicol prism, and then the two beams are brought into optical contact by a special rhomb similar to that shown in Fig. 14, for the Vierordt instrument. The intensity is changed by a second Nicol, the angular rotation of which can be measured, and, if again θ be the angle of rotation necessary to bring about equality of the two spectra in the field of view, $\frac{I}{I_0} = \cos^2 \theta$.

The Hüfner spectrophotometer has recently been much improved by Twyman, who has succeeded in reducing the experimental errors to a very small value indeed. Twyman points out that the principal source of error lies in the fact that the rays of light in passing through the dispersing prism system are partially polarised. For this reason the beam which does not pass through the Nicol prism outside the slit will become partially polarised, and, therefore, will lose in intensity when the second or analysing Nicol is rotated. As a matter of fact this error is corrected to a certain extent by the use of the Hüfner rhomb owing to the fact that the principal planes of this rhomb and the dispersing prism are at right angles to one another. Twyman shows that by the use of a rhomb made of the same glass as the prism, and so cut that the angle of incidence on the face of the rhomb is the same as that on the prism face, the error is entirely eliminated, for the polarisation caused by the two, rhomb and dispersing prism, are then exactly equal and in planes at right angles, and thus the two exactly counterbalance one another.

Further, the instrument is made with a constant deviation prism so that the telescope and collimator are fixed and the spectrum caused to pass across the field of view by the rotation of the prism, the principle being the same as that of the spectrometer shown in Fig. 4. The accuracy obtained with this improved form of spectrophotometer is exceedingly great and far superior to that obtained with the ordinary form of instrument. In actual practice the instrument is adjusted as follows. The best source of illumination is a Nernst filament lamp, and the rays from this are directed into the instrument, and the analysing Nicol prism is set at the zero reading. Owing to the necessary loss of light caused in the one beam by the polarising Nicol the two beams will naturally appear of different intensities. In order to correct this error a wedge of neutral tinted glass is mounted outside the slit in the path of the brighter beam. This wedge is slowly moved until the two spectra appear exactly equal in intensity in the field of view. The instrument is then in adjustment, and in determining the extinction coefficient of a given solution, the solution is put in an absorption cell with a Schultz corrector, and this is properly mounted in front of the polarising Nicol and slit. When the analysing Nicol has been rotated so as to bring the two spectra again to equality, and as stated above, the angle of rotation is θ, the ratio of the intensities of the two beams I/I_0 will be given by $\cos^2 \theta$.

In addition to the above-mentioned types of spectrophotometer, which are particularly adapted to the quantitative measurement of absorption since only one source of light is used, there have been several instruments devised more suited to the spectrophotometric comparison of two different light sources. These are more suited to spectropyrometry or the measurement of temperature by comparison of the emission spectrum of the body, the temperature of which has to be measured with that of some standard source. One of the most convenient of these instruments has been devised by Brace, and a diagrammatic arrangement is shown in Fig. 15. A and B are two exactly similar right-angled prisms which are cemented together. Before they are cemented, however, that surface of B which is to be cemented to A is heavily silvered, and this coating is carefully removed so as to leave a narrow horizontal strip across the centre of the prism face. The two prisms are then cemented together. One source is placed at C and the other at D, the rays from each passing through a slit and collimating lens. The rays from C are refracted at the first surface of A as shown, and pass through the junction of the two prisms above and below the silver strip. The rays from D enter the prism B and are reflected from the silver strip. Both beams undergo exactly the same amount of deviation, with the result that when brought to a focus a strip of spectrum from D will be seen between two strips of spectrum from C. When these are brought to equality the boundary lines between them disappear. The necessary variations in intensity may be brought about either by altering the slit-width, as in Vierordt's instrument, or by the use of a rotating sector with openings of known size placed in front of the light source.

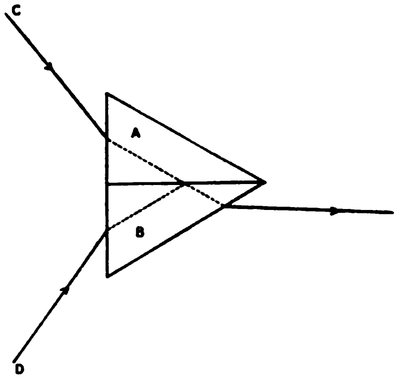


FIG. 15.

It is hardly necessary to point out that spectrophotometric measurements with ordinary instruments are limited to the visible region, and therefore only those substances the absorption bands of which lie in the visible region can be dealt with. Although H. A. Krüss has described a method by means of which two intensities in the ultra-violet can be photometrically compared by the use of a fluorescent screen, yet this seems to be incapable of extensive use, seeing that the brightness of the fluorescence is generally so small.

It would seem that the only method of

comparison is by photography. This comparison by photography must of necessity be very tedious, because it involves taking a series of photographs of the two spectra, the intensity of the standard spectrum being reduced by a known amount in each case. From a comparison of the resulting negatives the particular intensity of the standard required can be found.

The possible applications of spectrophotometry to the estimation of substances with absorption bands in the visible region, as may readily be understood, are very numerous. In the bibliography dealing with this section will be found references to many of these applications, for they are too numerous to describe in detail.

IX. **Qualitative and quantitative estimation of blood.** Blood contains the highly complex iron-containing crystalline colouring matter called hæmoglobin. This hæmoglobin has the power of readily linking itself to an atom of oxygen, which is in such a labile state that it can readily be given up and oxidise the waste products of the tissues of the body. While living blood generally contains both the oxygenated and the deoxygenated hæmoglobin, the former is essentially a constituent of arterial, and the latter of venous, blood. This labile oxygen may, therefore, be considered as the respiratory oxygen of the animal system. Hoppe-Seyler has shown that hæmoglobin is decomposed by acids, and by alkalis in the absence of air into hæmochromogen (sometimes called reduced hæmatin), and finally into hæmatin. This process is apparently a hydrolysis, whereby an albumen, globin, is split off. If in this process hydrochloric acid be used, an intermediary product known as hæmin is formed, which is the hydrochloride of hæmatin (see BLOOD). Again, if hæmatin is heated with concentrated nitric acid or is dissolved in concentrated sulphuric acid, it dissolves, giving a solution of hæmatoporphyrin. This substance contains no iron, the iron atom having been withdrawn as a ferrous salt from the hæmatin. According to Nencki and Sieber the following equation expresses the preparation of hæmatoporphyrin from hæmatin—

$$C_{32}H_{30}N_4FeO_3+3H_2O=C_{32}H_{34}N_4O_6+Fe.$$

Two reactions of hæmoglobin are of considerable importance, namely its oxidation and its reaction with carbon monoxide. When oxidised by a mild oxidising agent such as nitrites or potassium ferricyanide it is converted into a brown substance, methæmoglobin, the same substance being produced when hæmoglobin is exposed to air, as may be seen on the edges of wounds and on blood stains on cloth, &c.

The second reaction of hæmoglobin is the power which it possesses of absorbing carbon monoxide, a new compound being produced called carbon monoxide hæmoglobin. This is of great importance in dealing with cases of carbon monoxide poisoning.

The various derivatives of hæmoglobin may be prepared as follows: The blood is first defibrinated and diluted with 1 p.c. of caustic soda, when it is found to show the spectrum of oxyhæmoglobin. To reduce this back to hæmoglobin we may use freshly-prepared ammonium hydrogen sulphide, or better still, hydrazine hydrate, since in this case only nitrogen and water are formed

$$NH_2{\cdot}NH_2+O_2=N_2+2H_2O.$$

The addition of a few drops of concentrated potassium ferricyanide solution to diluted blood shows at once the spectrum of methæmoglobin.

If a drop of blood be warmed on a slide with one or two drops of glacial acetic acid and the mixture boiled over a small flame and then allowed to evaporate, the residue, when examined under the microscope, will show reddish-brown crystals of hæmin, known as Teichmann's crystals. Even an old blood stain gives the same, but better results are obtained in such a case if a small crystal of sodium chloride is added.

To prepare hæmin on a large scale, 1 volume of defibrinated and strained blood is added to 4 volumes of glacial acetic acid previously heated to 80°. As soon as the temperature has fallen to 55°–60°, the blood is again heated to 80°, and on cooling the crystals of hæmin separate out with characteristic silky lustre and dark-blue colour. These are allowed to settle for 12 hours, then decanted and washed with water, after which they are filtered off and washed with alcohol until the runnings are no longer coloured.

If the crystals are dissolved in very dilute caustic potash and then heated with dilute hydrochloric acid hæmatin is precipitated. This is then washed with water until free from chlorine.

Both hæmatin and hæmin dissolve in cold concentrated sulphuric acid to give hæmatoporphyrin, which is precipitated on the addition of water. The absorption spectra of the different colouring matters are as follows:—

Oxyhæmoglobin shows two absorption bands in dilute solution which coalesce into one band when the solution is more concentrated.

Formánek	5880–5650A	5550–5260A
Naumann	5890–5680A	5570–5270A (maximum at 5500)

In stronger solution one band at 5940–5180A.

Hæmoglobin. This only shows one band as a rule, though in very dilute solution a weaker band has been described as appearing on the red side.

Preyer (1871)	. 5980–5400A (maximum at 5520)
Gamgee (1880)	5950–5380A (maximum at 5500)
Formánek	. 5930–5700A and 5700–5400A.

Carbon monoxide hæmoglobin. Formánek describes two bands, 5810–5610A and 5500–5230A.

Methæmoglobin. The neutral or faintly acid solution is chocolate-brown, whilst when made alkaline with ammonia it turns red. The former shows a well-marked band in the red, and two others which are very weak and may not be seen. The latter gives a principal band nearer to the blue and two faint bands. The fainter bands in both cases seem to agree with those of oxyhæmoglobin.

Neutral or faintly acid bands, Formánek, 6400–6250A, 5780–5680A, and 5540–5300A.

Alkaline, Ziemke and Müller, 6050–5890A, 5890–5790A, and 5580–5350A.

Hæmatin. Alkaline solutions are red and acid solutions brown—

Alkaline solution (Naumann) . 6240–5750A.

Acid solution shows a principal band in the red and a weaker one—

Naumann . .6600–6300A and 5890–5270A.

Hæmatoporphyrin. Acid alcoholic solutions are purple to bluish-violet. Alkaline solutions are red to red with a violet tinge—

Acid, 2 bands (Naumann), 6060–5910A and 5890–5440A.

Alkaline, 4 bands (Formánek), 6330–6160A, 5890–5660A, 5200–5350A, and 5200–4980A.

For the quantitative estimation of blood the following values of the absorption ratios of oxyhæmoglobin, hæmoglobin, and carbonic oxide hæmoglobin may be given for the spectral regions specified (Hüfner).

Substance	Limits of spectral region	Absorption ratio
Oxyhæmoglobin . .	5650–5540A	0·002070
„ . .	5425–5315A	0·001312
Hæmoglobin . . .	5560–5540A	0·001354
„ . . .	5425–5315A	0·001778
Carbonic oxide hæmoglobin	5650–5540A	0·001383
„ „ „ .	5425–5315A	0·001263

In the detection of blood stains, such as may occur in medico-legal cases, the stain is either washed out with water or digested with warm 10 p.c. sodium carbonate solution. The spectrum is noted and then the solution is treated with a reducing agent, for example ammonium hydrogen sulphide or hydrazine hydrate, as described above, when the spectrum of hæmoglobin is formed. This is an exceedingly delicate test; shaking with air restores the original spectrum, but a fresh addition of the reducing agent reproduces hæmoglobin.

Again the hæmin and hæmotoporphyrin test described above can be employed. In the detection of carbon monoxide poisoning the blood shows the spectrum of carbonic oxide hæmoglobin. This is somewhat similar to the oxyhæmoglobin spectrum, but it is quite unaltered by ammonium hydrogen sulphide, and in this manner may be sharply differentiated.

X. **Optical Pyrometry.** An important application of the spectroscope lies in the measurement of the intensity of the radiation from an incandescent source by direct comparison with that of a standard, for by this means the temperature of the former may be arrived at. Generally this comparison is carried out for red light, because, in the first place, the colour of the light emitted by a body varies very considerably with the temperature, and in the second place it allows the measurements to be made at lower temperatures. It must be remembered that the intensity of the radiation emitted by an incandescent substance is not only a function of the temperature, but also that it depends upon the surface and composition of the substance. In dealing with the radiation from any substance it is necessary, therefore, to set up a standard in terms of which all radiation laws can be expressed. This was first done by Kirchhoff, who defined the absolutely 'black body' as that which would absorb every radiation without reflection or transmission. He pointed out that the radiation of the 'black body' is purely a function of the temperature. Although no substance is known the surface radiation of which is exactly equal to that of the 'black body,' yet it is possible almost to realise the condition by maintaining a vessel at a constant temperature, and observing the radiation from the inside through a small hole in one of the walls. For high temperatures a porcelain tube may be electrically heated to a known temperature (determined by a thermocouple) and the radiation from the central portion examined. Such an apparatus is used in the calibration of optical pyrometers. It follows that in the optical measurement of temperatures the instrument will always give the 'black body' temperature corresponding to the intensity radiation dealt with. This temperature will, of course, only be the true temperature of the incandescent body when the latter is behaving as a 'black body.' Such a condition may frequently be realised, as, for example, in the determination of the temperature of a furnace by the examination of the radiation from the inside of a porcelain or metal tube projecting into the furnace. If, however, the 'black body' conditions are not obtained the optical pyrometer will usually give a temperature lower than the true value. In technical processes this error may not be of great importance, as, for example, when it is only necessary to reproduce certain given conditions with accuracy at any moment.

Before dealing with the methods of working with the various forms of optical pyrometers it is necessary to speak of the laws of radiation. The Stefan-Boltzmann law states that the total radiation emitted by the 'black body' is directly proportional to the fourth power of the absolute temperature, and may be expressed as follows:—

$$I = k(T^4 - T_0^4),$$

where I is the total radiation from the black body at the absolute temperature T to the body at the absolute temperature T_0, and k is a constant. It is well known that as the temperature of a body changes the wave-length of the maximum of the radiation varies, and Wien concluded that, if λ_m be the wave-length of the maximum energy, $\lambda_m T = $ a constant. Combining this with the Stefan-Boltzmann law, Wien obtained the relation $I_{max} T^{-5} = $ constant, where I_{max} is the energy corresponding to the wave-length λ_m and T is the absolute temperature of the 'black body.'

Even although these relations were deduced for the 'black body' they hold good for other radiating surfaces, but, of course, the values of the constants are different. Wien's second equation is then modified to $I_{max} T^{-a} = $ constant.

Some further investigations of Wien led him to the following equation:—

$$I = b\lambda^{-5} e^{-\frac{c}{\lambda T}},$$

where I is the energy corresponding to the wave-length λ, e is the base of natural logarithms, T is the absolute temperature, and b and c are constants. Although it has been found that this expression does not hold good over long ranges of wave-lengths, yet it is sufficiently accurate for the ranges dealt with in optical pyrometry, and may be used for the calibration of these instruments. In practice the method of work with the optical pyrometer is as follows: Some standard of illumination is chosen, and the intensity of the red light of chosen wave-length emitted by the incandescent body is varied by some means until it becomes equal to that of the standard. For the calibration of this type of pyrometer Wien's third equation may be used—

$$I=b\lambda^{-5}e^{-\frac{c}{\lambda T}}.$$

This may be written—

$$\log I=\log b-5\log\lambda-\frac{c}{\lambda T}\log e$$

or

$$\log I=C+\frac{K}{T}$$

where $C=\log b-5\log\lambda$, and $K=-\frac{c}{\lambda}\log e$.

Evidently, since we are dealing with the radiation of only one wave-length, there is a linear relation between log I and 1/T. The instrument may be calibrated, therefore, from measurements of I at two known temperatures. A similar relation will hold good if the radiation be not that of the 'black body,' but the constants C and K will then be different.

In the Le Chatelier pyrometer the radiation from the incandescent source passes through an iris diaphragm, and is brought to a focus by a lens and examined through a screen of red glass with a Ramsden eye-piece. The rays from the standard of comparison pass down a tube at right angles to the first tube, and are reflected from a plane mirror into the eye-piece. The equality between the two radiations is produced by altering the aperture of the iris diaphragm. If the radiation from the incandescent body is too great one or more plates of tinted glass are introduced, the coefficients of absorption of which are known, and the final adjustment done by the iris diaphragm. The effective aperture of this diaphragm can be obtained from the scale reading.

In the Wanner pyrometer the principle is the polarisation of both rays, as in the case of the Glan spectrophotometer described above. The radiations from the two sources are focussed on to two adjacent slits, and then after being rendered parallel by a collimating lens they pass through a direct vision prism system. They then pass through a Rochon prism which resolves each beam into two portions polarised at right angles to each other. By means of a biprism and lens two red images oppositely polarised, one from each source, are focussed contiguous to each other on a third slit. The two beams then pass through a Nicol prism into the eye-piece. If the two intensities be equal, and the Nicol set at 45° with the plane of polarisation of each, both will appear of equal brightness. If, however, the two intensities be not equal, they may be equalised in the field of view of the eye-piece by rotating the Nicol. If the necessary angle of rotation of the Nicol is θ, the ratio between the intensities will be given by—

$$\frac{I_1}{I_2}=\tan^2\theta.$$

For the standard source of light in these instruments a Hefner standard amyl acetate lamp, a gasoline lamp, or an electric filament lamp fed with constant current may be used.

In the Féry instrument the total radiation from the incandescent object is measured. The rays are focussed upon a sensitive thermocouple, and the energy of radiation determined from the readings of a galvanometer connected with the thermocouple. In the calibration of this instrument the Stefan-Boltzmann law is employed. *V.* PYROMETRY.

XI. Absorption spectra and chemical constitution. In dealing with the absorption of radiant energy exerted by chemical substances it may be pointed out that the observations which have been made extend over a very long range. Whereas, perhaps, the most familiar results are those which have been obtained in the visible region, the observations have been pushed to the extreme limit of $\lambda=1200$A in the ultra-violet on the one hand, and on the other to a great distance in the infra-red ($\lambda=15000$A). Now, whatever may be the view taken of the origin of absorption bands, there is little doubt that selective absorption in the infra-red is due to a different cause from that of the absorption in the visible and ultra-violet regions. This may at once be understood from the fact that characteristic absorption bands in the infra-red may be traced to definite atomic groupings, while such is by no means the case as regards the ultra-violet absorption bands. It has been found that the OH group and the SO_4 group, for example, always exhibit characteristic absorption bands in the infra-red. Since the extreme infra-red region is beyond the limits of vision and of photographic sensibility it is necessary to employ a bolometer, radiometer, thermopile, or radiomicrometer, and to measure the intensities of the radiant energy at any given point of this heat spectrum by its means. although it may be remembered that, as has been said above, it has been found possible to obtain photographic records far beyond the limit of visibility.

A great number of observations have been made upon infra-red absorption by Abney and Festing, Spring, Puccianti, and others, but it can hardly be said that many conclusions can be drawn from the work of these investigators as regards the relation between absorption and constitution. Coblentz, however, has published some important results on infra-red absorption in relation to constitution. It was found by him that the following atomic groups exhibit characteristic absorption bands at the positions specified.

Compounds having the following groups	Show characteristic absorption bands at
CH_2 or CH_3 .	3·43, 6·86, 13·6, 13·8, and 14μ
NH_2 . .	2·96, 6·1–6·15μ
C_6H_6 . .	3·25, 6·75, 8·68, 9·8, 11·8, 12·95μ
NO_2 . .	7·47, 9·08 (?)μ
OH . .	3·0μ
NCS . .	4·78μ
SO_4 . .	4·55, 8·7, 9·1μ

where $\mu=0{\cdot}001$ mm.$=1000$ A.

A large portion of Coblentz's observations dealt with minerals and other compounds containing hydrogen and oxygen, and it was always found possible at once to determine whether the hydrogen and oxygen exist as water of crystallisation. Water exhibits absorption bands at 1·5, 3, 4·75, and 6μ, and these bands are always shown when the compound contains water of crystallisation. The band at 3μ is due to the OH group in the water, and if the compound only contains the OH group, and not water of crystallisation, this band only is observed. A single exception was noted, namely cane sugar, which shows distinct evidences of the water bands, and so the absorption would indicate that in this substance some of the hydrogen and oxygen exist as water and not entirely as hydroxyl or water of constitution. It is interesting that this substance is the only exception amongst a great number that were examined.

The chemical evidence against this conclusion is, of course, overwhelmingly strong, but at the same time the argument based on the presence of the absorption bands of water cannot be lightly laid on one side. Coblentz, in addition to cane sugar, has investigated the absorption of *d*-fructose, *d*-glucose, maltose, lactose, raffinose, and gum-arabic. Of these latter *d*-fructose is the only one which does not possess water of crystallisation, and, indeed, is the only one which shows no trace of the water bands. This disposes of the possible contention that the number of hydroxyl groups in the carbohydrate molecule might conceivably give rise to bands similar to those of water.

The results of the observation of the absorption of talc and serpentine were very interesting, and confirm the chemical conclusions, for talc shows no evidence of the hydroxyl band at 3μ, whilst serpentine shows a large band at this point. Coblentz concludes from his examination of a number of silicates that, as no characteristic band is traceable to them, the union of the silicate radicle is different in each mineral containing it.

The results obtained by Coblentz show very conclusively that the absorption bands in the infra-red are due to specific atomic groupings. In the case of absorption in the visible and ultra-violet regions it is equally manifest that the absorption bands cannot be attributed to groups of atoms as such, because the position and character of the bands are profoundly modified by a single substitution process. For example, benzene in alcoholic solution gives eight absorption bands in the ultra-violet, while nitrobenzene in the same solvent gives only the merest trace of a single broad band. On the other hand, phenol and aniline give very well-marked and broad absorption bands just beyond the visible region. No characteristic absorption, for example, therefore, can be attributed to the C_6H_5 group, seeing that the last three bodies differ so much in their absorption spectra.

It appears that selective absorption in the ultra-violet is due in the main to the presence of unsaturation in the molecule. For example, it has been found that a saturated hydrocarbon does not show any selective absorption. The paraffin hydrocarbons only exhibit general absorption, which extends further and further towards the red with increase of molecular weight. This is also true for the fatty acids and their esters, and for the alcohols derived from the paraffin series, although there is a slight increase in the general absorption in each case compared with the corresponding hydrocarbon.

The introduction of unsaturated groups tends to increase the amount of general absorption, and in some cases to cause the appearance of selective absorption in the ultra-violet region. Thus, for example, the ketone group in acetone and its homologues and in compounds of the type of acetylacetone and ethyl acetoacetate causes the appearance of well-marked absorption bands.

The same is true as regards the saturated hydrocarbons of the aromatic series, for *cyclo*-hexane does not show any more than slight general absorption. Similarly benzene hexachloride ($C_6H_6Cl_6$) only shows general absorption. On the other hand, benzene itself shows strong selective absorption with as many as eight absorption bands. Again naphthalene, phenanthrene, and other condensed ring hydrocarbons also show complicated banded absorption. The absorption of all these compounds tends to diminish and the bands to disappear as the compounds are reduced and become more saturated.

The substitution of one of the hydrogen atoms of the benzene ring by a halogen atom or group of atoms very profoundly modifies the absorption, and the type of spectrum now shown depends upon the nature of the substituent atom or atoms. Thus chlorobenzene shows seven bands which are in quite different positions from those of benzene. The substitution by methyl or any saturated radicle produces a spectrum showing one of the benzene bands, while the others are amalgamated into one broad band. The hydroxyl, amino, and other ortho-directing groups produce one broad and persistent band which is nearer the red than the bands of benzene itself. The nitro group, on the other hand, almost entirely obliterates the selective absorption of benzene and shows strong general absorption with only a very shallow band.

There seems to be no hard-and-fast rule as regards the type of absorption induced by the substituent group, for benzaldehyde shows a small band nearer the red than the one in nitrobenzene; and, further, benzene sulphonic acid shows several well-marked absorption bands.

The aromatic nitrogen bases, such as pyridine, quinoline, &c., all show well-marked absorption bands.

When the benzene ring is associated with groups possessing strong residual affinity such as, for example, is the case in azobenzene or in cinnamylideneacetone

$$C_6H_5\cdot CH:CH\cdot CH:CH\cdot CO\cdot CH_3$$

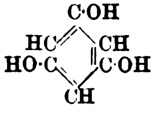
the position of the absorption bands, compared with those of benzene, is shifted towards the red, so that they may lie in the visible region, with the result that the compound appears visibly coloured. Visible colour may, therefore, be said to arise from the association together of unsaturated groups in the molecule. The benzene ring possesses a type of residual affinity that is peculiarly suited to this purpose, and so the aromatic compounds are more frequently coloured than the aliphatic compounds.

It does not seem to be absolutely necessary that the associated centres of unsaturation be present within the same molecule, for it is possible in certain cases to obtain the shift of the absorption bands into the visible region by the intimate mixture of suitable compounds, such mixtures frequently developing striking colours. Such intimate mixtures are produced by dissolving one substance in the other, when, as may be understood, the residual affinities may mutually influence one another in very much the same way as if they were present within the same molecule. It is manifest from this that the influence of the solvent is of extreme importance in absorption spectra observations, and it is a frequent occurrence to find that the absorption spectrum of a substance in one solvent is very materially different from what it is in the case of another solvent. Although great care must be taken, therefore, to guard against errors arising from the influence, yet it may at once be said that absorption spectra observations are capable of throwing great light upon the problem of chemical constitution, and there are now many cases known in which the constitution has been settled when the chemical evidence has failed. Further than this, it may be said that since the presence of absorption bands must be traced to the play of forces between the centres of residual affinity within the molecule, so there must be expected an intimate relation between absorption and chemical reactivity. This intimate connection has been proved in many cases, and it is not too much to hope that absorption spectra will serve to advance very materially the study of chemical reactions.

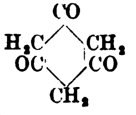
It has already been emphasised how important an influence the solvent may have upon the absorption spectrum given by a compound in solution, arising from the fact that the residual affinities of the two may form a combined system such as occur when such residual affinities are present within the same molecule. It follows at once that the conclusions drawn as regards the constitutions of compounds from the similarity of their absorption with that of their derivatives of known constitution can only be looked upon strictly as being definite for the compounds when in solution in the chosen solvent. This, however, for two reasons, need not cause apprehension, for, provided that the solvent used be one of no very decidedly marked residual affinity, there is no reason to expect that any error will be involved by the assumption that the constitution is the same for the pure substance itself. Alcohol is a very safe solvent to use, because, with perhaps the exception of hexane and heptane, it has the least effect upon the systems of residual affinities present in the molecules of the compounds dissolved in it. In all the cases given below alcohol was used unless another solvent is specifically mentioned.

Many cases are known in which it has been found possible to elucidate the chemical constitution of substances by comparing their absorption with that of an analogous compound of perfectly known constitution, and the following examples may be given :—

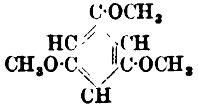
Phloroglucinol may be expressed by either of the two following formulæ—



or



as far as the chemical evidence is concerned. Now, the constitution of the trimethyl ether of phloroglucinol is known to be—



The absorption curves of phloroglucinol itself and the trimethyl ether are shown in Fig. 16, and it may be seen that they are almost exactly similar, and therefore there is no doubt that the two substances are of similar constitution. or, in other words, phloroglucinol must exist in the trihydroxy form.

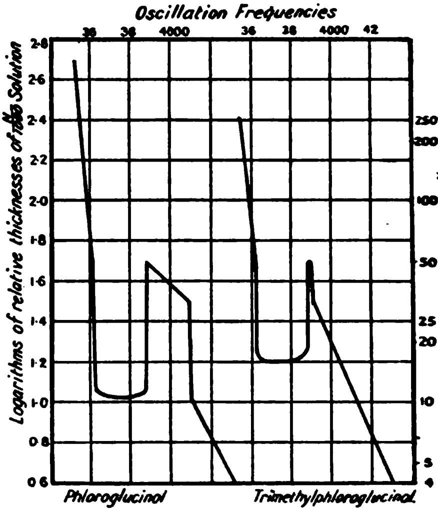
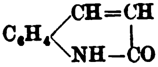


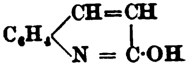
FIG. 16.

A second case is the proof of the constitution of carbostyril. Chemical evidence alone is not capable of differentiating between the two formulæ—



$$C_6H_4\left\langle\begin{matrix} CH=CH \\ | \\ NH-CO \end{matrix}\right.$$

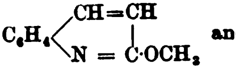
and



$$C_6H_4\left\langle\begin{matrix} CH=CH \\ | \\ N = C{\cdot}OH \end{matrix}\right.$$

The methyl ethers corresponding to the above possible formulæ are both known, namely,

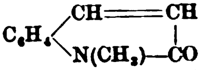
methylcarbostyril



$$C_6H_4\left\langle\begin{matrix} CH=CH \\ | \\ N = C{\cdot}OCH_3 \end{matrix}\right.$$

and

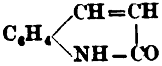
methyl*pseudo*carbostyril



$$C_6H_4\left\langle\begin{matrix} CH=\!=\!=CH \\ | \\ N(CH_3)-CO \end{matrix}\right.$$

The former of these is obtained by the action of methyl iodide and sodium hydroxide upon carbostyril in methyl alcohol solution, whilst the latter is prepared by the action of methyl iodide upon the silver salt of carbostyril.

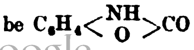
The absorption spectra of the two ethers are shown in Fig. 17, and the absorption curve of carbostyril is practically identical with that of methyl*pseudo*carbostyril. It therefore follows that the constitution of carbostyril is to be represented by the formula



$$C_6H_4\left\langle\begin{matrix} CH=CH \\ | \\ NH-CO \end{matrix}\right.$$

Although it might be urged that both forms may be present in dynamic equilibrium, still, even if this were true, the amount of the ketonic form must be far in excess of the enolic form.

In exactly the same way the constitution of *o*-oxycarbanil was proved to be



$$C_6H_4\left\langle\begin{matrix} NH \\ O \end{matrix}\right\rangle CO$$

for the absorption curves show that its constitution is the same as that of the lactam ether.

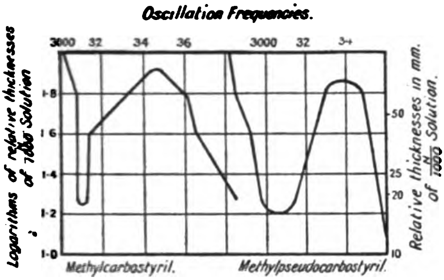


FIG. 17.

The constitution of the lactam and lactim ethers is known to be

$$C_6H_4<\overset{N(C_2H_5)}{\underset{O}{}}>CO \text{ and } C_6H_4<\overset{N}{\underset{O}{}}>C\cdot OC_2H_5$$

respectively.

The absorption curves of the two ethers is shown in Fig. 18.

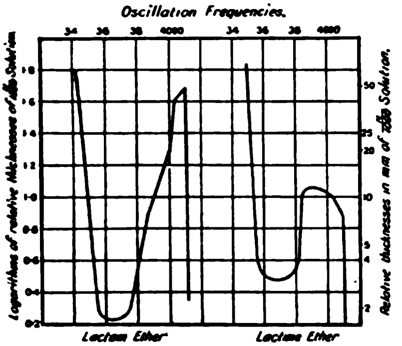
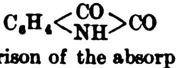


FIG. 18.

In a perfectly similar way isatin was proved to have the constitution represented by the formula—



$$C_6H_4<\overset{CO}{\underset{NH}{}}>CO$$

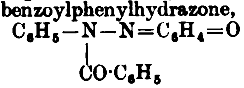
By a comparison of the absorption spectrum of cyanuric acid with those of the two possible methyl ethers, namely, methyl cyanurate and methyl *iso*cyanurate, it has been shown that cyanuric acid has a constitution analogous to the former substance. It may be pointed out, however, that none of these substances exhibit an absorption band, a fact which is not in harmony with a formula so analogous to that of pyridine and still more closely allied to that of dimethylpyrazine. It is, therefore, doubtful whether the constitution of cyanuric acid is rightly understood.

It may be seen at once that the above conclusions are based on the fact that no change in the absorption spectrum is produced when a methyl or ethyl group is substituted for a hydrogen atom. Although this has been shown to be true by Hartley in several cases which he examined, it is not true in every case. Exceptions are known, particularly in those cases where the hydrogen atom is labile or where the hydrogen atom is directly attached to the benzene ring. Basing his conclusions on somewhat similar evidence, Tuck has investigated the absorption spectra of the hydroxyazo compounds, and has been able to determine the constitution of these substances. In his first paper he dealt with benzeneazophenol and benzeneazo-*m*-cresol, both of which are *p*-hydroxyazo compounds. The absorption of these substances was compared with that of their benzoyl derivatives and their methyl ethers. The chemical evidence leaves no doubt that the methyl ethers and the benzoyl derivatives of these hydroxyazo compounds are true azo compounds, and that their formulæ are as follows—

Benzene azophenetole $C_6H_5{-}N{=}N{-}C_6H_4{-}OCH_3$
Benzoyl benzeneazophenol
$C_6H_5{-}N{=}N{-}C_6H_4{-}O{-}COC_6H_5$.

The close similarity between the absorption of the parent substances and that of the ethers and benzoyl derivative shows conclusively that these parent substances are true hydroxyazo compounds, and have formulæ of the type $C_6H_5-N=N-C_6H_4OH$, and not $C_6H_5-NH-N=C_6H_4=O$.

This conclusion is strengthened by the fact that the absorption of the corresponding quinone phenylhydrazone derivatives is quite different. The compound investigated was *p*-benzoquinonebenzoylphenylhydrazone, which has the formula



$$C_6H_5-\underset{\displaystyle CO\cdot C_6H_5}{\underset{|}{N}}-N=C_6H_4=O$$

In the case of the corresponding *o*-hydroxyazo-compounds Tuck found that these are *o*-quinone phenylhydrazones. The actual compounds examined were benzeneazo-*p*-cresol and *p*-tolueneazo-*p*-cresol, their methyl ethers and benzoyl derivatives. The absorption curves of the ethers agree with those of the ethers of the *para*-compounds and with that of azobenzene. This was to be expected, as the chemical evidence has proved them to be azo derivatives. The benzoyl derivatives, on the other hand, give very different spectra, and their curves show a very marked and close relationship with that of benzoquinone benzoylphenylhydrazone. There is no doubt, therefore, that these benzoyl derivatives are in the quinone hydrazone form. Since the absorption curves of the parent substances show a marked agreement with those of their benzoyl derivatives and considerable disagreement with those of their ethers, it may be concluded that the parent compounds are quinone hydrazones, and are derivatives, therefore, of *o*-benzoquinone $C_6H_5-NH-N=C_6H_4=O$.

One of the most important theories of the colour of organic compounds is that known as the quinonoid theory. It is well known that *p*-benzoquinone is a strongly yellow coloured substance, and the general theory has generally been held that visible colour of compounds, especially aromatic compounds, is to be explained by their having a quinonoid structure, that is, they contain the linking $=\!<\!\equiv\!>\!=$. It may be seen at once that this theory only takes account of visible colour. Now, every compound which exhibits selective absorption is coloured in the physical sense, and it would seem therefore that any attempt to connect visible colour with a particular structure need not necessarily be sound. It has already been stated that the association of residual affinities tends to shift the absorption bands towards the red, and it follows that if the centres of unsaturation are sufficiently strong in character and suitably associated, the absorption band can easily be caused to shift into the visible region with a result that the compound will become visibly coloured.

Evidently, therefore, there is no necessity for the assumption of the quinonoid structure in order to account for visible colour, though clearly such a structure may give rise to it. There is a tendency on the part of organic chemists to write a quinonoid structure wherever it is possible in order to account for visible colour; but it may be said at once that spectroscopic observations have shown that this quinonoid hypothesis is entirely unnecessary, and have indeed proved that the particular substances examined do not exist in the quinonoid form.

As a definite example of the association of residual affinity with the production of visible colour without any possibility of a quinonoid configuration, the diketone diacetyl may be quoted; the absorption spectrum of this substance is shown in Fig. 19, and owing to the association of the two CH_3CO groups, each of which alone shows selective absorption (compare the monoketones of the aliphatic series), the absorption band appears in the visible region and the substance is yellow. The case of camphor quinone is perfectly analogous. The following results show clearly that the quinonoid theory is entirely fallacious and unnecessary as regards visible colour.

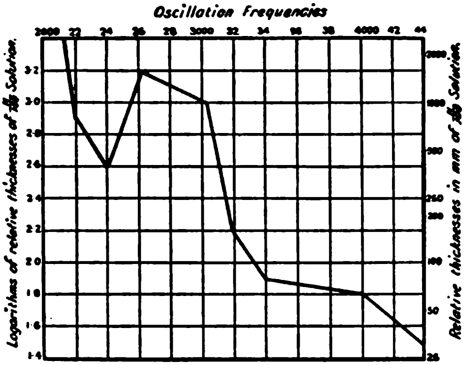


FIG. 19.

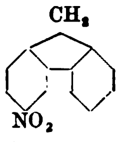
It was pointed out above that benzene and the condensed ring hydrocarbons of the aromatic series show complicated absorption spectra with many bands. There is little doubt from the chemical evidence that in the case of benzene the carbon ring is perpetually in a state of vibration, and it was suggested that the various absorption bands are in all probability due to phases in the configuration of the molecule produced by its vibrations. Although at the time only seven bands were described, while eight are now known, this does not invalidate the principle then put forward. It is evident that the vibrations of the molecule and the play of forces thereby resulting will be altered when the hydrogen atoms of benzene are substituted by other atoms or groups of atoms. This alteration may be due to two causes; firstly, the change in the vibration of the ring induced by the weight of the substituent group may play a part; and secondly, the change in the play of forces due to the mutual influence of the residual affinities of the benzene ring and of the substituent group must produce some effect. When the substituent group is of the ortho-directing type, such as OH or NH_2, the absorption band produced is always strongly marked, and is nearer to the red than are the bands of benzene itself. When phenol is dissolved in caustic soda solution, the increase in basicity resulting from the conversion of OH into ONa causes a still further shift of the band towards the red. An exactly similar shift towards the red is shown in the case of aniline when the basicity of the nitrogen atom is increased by the substitution of the amino hydrogen atoms by alkyl groups.

On the other hand, the substitution of the acid NO_2 group decreases very considerably the absorption of benzene, so that very small, if any, selective absorption is observed. This effect is due to the mutual influence of the benzene nucleus and the NO_2 group, which practically neutralise one another, with the result that a condensed system is formed, showing little or no selective absorption.

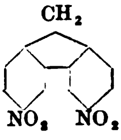
It would appear from the above that there must be almost perfect balance between the residual affinities of the C_6H_5 nucleus and the NO_2 group, and consequently the introduction of a second group into the benzene ring, and one which has an opposite character to that of the NO_2 group, will tend to destroy this balance with a result that the new compound will again show selective absorption.

This has been proved in the case of the three nitrotoluenes and the two mononitronaphthalenes, as well as for certain other compounds of the same type.

A very good test case was found in the mono-nitro and di-nitro fluorenes



and



for the former compound, where only one of the rings has a nitro group, should show a well-marked absorption band owing to the opening up of the closed system of the one ring by the residual affinity of the other. In the latter compound both rings have an NO_2 group, and as there is no unsaturated group present to open their systems up, this compound should exhibit no selective absorption. The absorption spectra of these two compounds agree perfectly with the prediction, for mono-nitrofluorene shows a strongly marked band, while the dinitro compound shows no band at all.

If the second group introduced into nitrobenzene be more markedly different from the NO_2 group, if, for example, the absorption of the nitroanisoles be considered, then the absorption bands are very decided, and are nearer to the red than in the case of the nitro-toluenes. The effect is still more marked in the case of nitroquinoldimethyl ether, which has two OCH_3 groups, for the absorption band is now so far shifted towards the red that the substance appears yellow to the eye.

An interesting point is to be noted with this compound, for its solution in hexane or a saturated hydrocarbon is colourless. This fact might at first sight tempt one to believe in a different structure for the compound in the two solvents alcohol and hydrocarbon. The absorption spectra of the two solutions, however, are very similar, the only difference being that the band is nearer the red in the case of the alcoholic solution. It happens that the band given by the alcoholic solution just lies within the limits of visibility, so the solutions appear coloured to the eye. The absorption band with the hexane solution lies just beyond the visible limit, and therefore the eye fails to detect any colour.

If, now, the second constituent group in nitrobenzene be still more strongly basic, the absorption bands of the resulting compounds will be still further shifted towards the red, with the result that these substances will be still more strongly coloured. Thus, for example, the absorption bands of *p*-nitrodimethylaniline is shown by the full curve in Fig. 20. It is evident from what has been said that this absorption band is due to the opening up of the condensed system of nitrobenzene by the strongly electropositive $N(CH_3)_2$ group. Almost exactly the same absorption as may be seen by the dotted curve in Fig. 20 is shown by para-nitroaniline itself, and consequently there is not the slightest possible doubt that the constitution of this body is the same as that of its dimethyl derivative. The constitution of the latter is of course $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>N{-}C_6H_4NO_2$ and therefore the parent substance must have the constitution $NH_2{-}C_6H_4NO_2$. This at once is opposed to the quinonoid theory. According to this theory, the constitution of the *o*- and *p*-nitranilines are to be represented by a quinonoid formula; that is to say, the formula of *p*-nitroaniline would be—

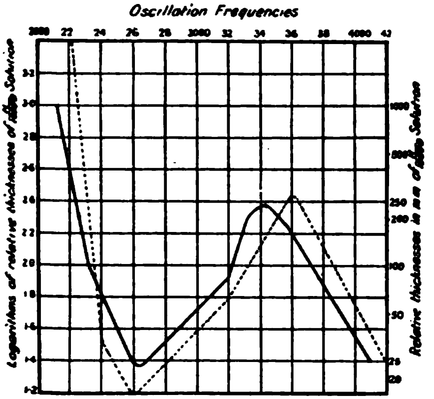
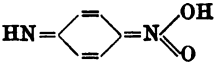


FIG. 20.



The quinonoid theory has also gained considerable support from the fact that *meta*-substituted compounds as a rule show less colour than that of the isomeric *ortho*- and *para*- bodies. As a static *meta*-quinone structure in a simple compound seems to be impossible the case for that structure of the *ortho*- and *para*-isomers was strengthened. Although it is true that the *meta*-compounds are less coloured, yet, generally speaking, their absorption curves show bands similar to those of the *ortho*- and *para*- substances, though they are less pronounced. As a result of this it is evident that the upholders of the quinonoid theory ought to accept a quinonoid structure for these *meta*-derivatives. As a matter of fact, however, the absorption band of *meta*-nitrodimethylaniline is distinctly nearer to the red than the band of *meta*-nitroaniline itself and so the substance is still more strongly coloured. This of course is due to the fact that the basicity of the nitrogen atom has been increased by the substitution of its hydrogen atom by the methyl groups, and the shift of the absorption band is exactly analogous to the shift observed on methylating aniline, as has already been noted.

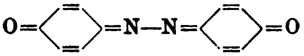
The three nitroanilines and their dimethyl derivatives therefore show exactly analogous absorption, and clearly they must possess the same constitution.

The explanation of the absorption and colour of these six compounds must be the same, and so it must be concluded that all three nitroanilines cannot have a quinonoid structure.

Exactly similar conclusions must be drawn respecting the constitution of the nitrophenols and their sodium salts. A comparison of the absorption of the nitrophenols with that of their corresponding methyl and ethyl ethers shows at once that the nitrophenols themselves are certainly not quinonoid. The change in colour observed when these substances are treated with sodium hydroxide must be due simply to the shift of the absorption band towards the red which is always produced when a phenol is converted into its sodium salt. As has already been said, phenol itself shows the same shift in its absorption, and, moreover, the absorption of sodium phenoxide is the same as that of aniline.

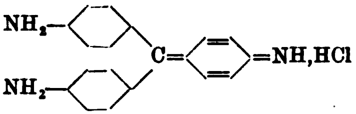
The similarity between the absorption of the sodium salts of the nitro-phenols and the corresponding nitro-anilines is very decided, and consequently there is no room for any doubt that the sodium salts of the nitro-phenols do not exist in quinonoid form. This conclusion is emphasised by the fact that the absorption spectrum of the nitro-phenols and their salts do not show that marked difference in character which would of necessity ensue if such a radical difference in constitution existed as required by the quinonoid hypothesis.

The quinonoid theory has been used to explain the colour of the alkali metal salts of such compounds as the nitro-benzene azophenols and the nitro-benzene azo-*a*-naphthols. The spectroscopic examination of these substances, using the same argument as detailed above, shows quite clearly that these substances do not exist in the quinonoid form. As conclusive evidence in support of this it is to be noted that *p*-benzoquinone azine—

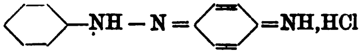


exhibits an absorption curve which is absolutely and entirely different from that given by any of the above compounds.

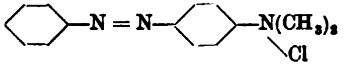
One of the most important applications of the quinonoid theory is the explanation by its means of the colour of the dye-stuffs. Perhaps the most familiar case is that of *para*-rosaniline hydrochloride with the suggested formula—



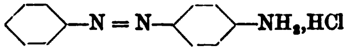
Similar quinonoid formulæ have been suggested for the other dye-stuffs of this type. Again, the same theory has been applied to the azo-dyestuffs which contain the azo-linking and one or more amino groups. Such a structure may be exemplified by that proposed for the hydrochloride of *p*-amino azo-benzene—



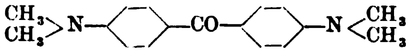
and in this case the formula has been supported by the fact that the absorption of the above salt bears no resemblance to that of—



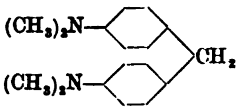
so that the hydrochloride does not seem to exist in the form



Some investigations, however, into the influence of acid upon aromatic bases such as the aminoaldehydes and aminoketones show that the above quinonoid formulæ are unnecessary and improbable. It has been found that the addition of small quantities of hydrochloric acid to the alcoholic solution of these bodies produces a very marked coloration which gives rise to a new absorption band in the visible region. It is necessary that less than one equivalent of hydrochloric acid be added for the colour to be produced, and the addition of a further quantity of acid destroys the colour and forms the true hydrochloride. These colours are due to the formation of an intermediary phase through which the base passes before its conversion into the salt. This intermediary phase is perfectly stable in the presence of the small quantity of acid. In the case of a mon-acid base such as *p*-aminobenzaldehyde, ½ eq. of HCl produces the best results. With a di-acid base as Michler's ketone (tetramethyl diaminobenzophenone)—



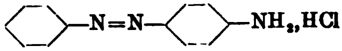
one equivalent of acid is best. As it is known that the coloured compound is not a true hydrochloride, therefore in this latter case it must be concluded that the hydrochloric acid distributes itself equally between the two nitrogen atoms. The analogy with rosaniline hydrochloride is quite apparent, for in this salt the affinity of the acid radicle influences all the nitrogen atoms, and so the colour is due to the fact that the intermediate phase happens to exist as a stable crystalline substance. This view is borne out by the fact that the trihydrochloride has far less deep a colour than the monohydrochloride. Again, it must follow if this view be correct that it should be possible to produce a highly coloured intermediate phase of the leuco base of a dye by means of a suitable acid solvent. Such, indeed, can be done, for if the leuco base be dissolved in nitrobenzene the solution is highly coloured. For example, if the leuco base of malachite green



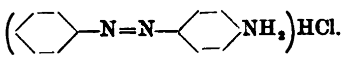
be dissolved in nitrobenzene the solution shows a magnificent red colour, which is discharged on dilution with alcohol.

Exactly the same arguments apply to the aminoazo colours, for in these bodies there are present at least two basic groups amongst which the acid radicle distributes itself with the formation of an 'intermediate phase,' which is a stable crystalline substance.

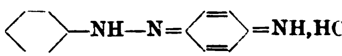
If a solution of azobenzene is treated with hydrochloric acid, the absorption spectrum will change, and a new absorption band will be obtained nearer to the red than that of azobenzene itself. The phenomenon doubtless is due to the same cause as in the case of the aminoaldehydes and ketones mentioned above, the only difference being that owing to the far less pronounced basic character of the nitrogen atoms a much greater concentration of acid is required. In the case of the aminoazo compounds when in acid solution a much less concentration of acid is required, since the amino group acts as a 'carrier,' and the affinity of the acid then is distributed between the amino and azo groups with the formation of the highly coloured intermediate phase. It has already been pointed out that the formula of the hydrochloride of aminoazobenzene cannot be expressed by the static formula—



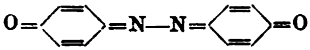
but, as now may be understood, the formula is preferably to be written—



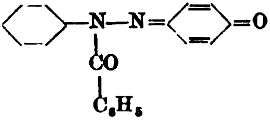
The quinonoid formula



may be ruled out, of course, because the absorption spectrum given by aminoazobenzene hydrochloride bears no resemblance to that of either of the similar substances which are known to possess a quinonoid structure, namely,



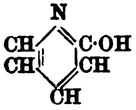
and



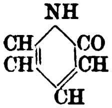
These two substances have already been dealt with above.

These foregoing arguments might be extended considerably and applied to many other compounds, the colours of which have been explained by the quononoid hypothesis, but sufficient has already been said to show that this conception is either entirely negatived or rendered quite unnecessary and improbable in every case where the spectroscope has been applied. In the bibliography dealing with this particular branch of spectroscopic work a very complete list of papers is given, and perhaps a seeming discrepancy may be pointed out so as to guard against a possible misconception. In the earlier stages of the investigation dealing with the absorption of the nitrophenols and the nitranilines the results obtained were interpreted as being in favour of the quinonoid theory, and it was not for some time that the conclusion was definitely arrived at that these previous arguments were unsound. This recantation, together with the definite proofs in favour of the views detailed above, was published in 1910.

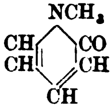
The absorption spectrum of pyridine and its derivatives give some considerable support to the view advanced above of the vibrations of the ring in the aromatic compounds. As was first shown by Hartley, pyridine gives an absorption band with its head at $\frac{1}{\lambda}=3900$, and the addition of hydrochloric acid to the solution enormously increases the depth or persistence of the band without changing its position. Later observations show that this is also true with the picolines and with lutidine. The vibrations present in the benzene ring are modified and restrained by the residual affinity of the nitrogen atom, which has been substituted for one of the carbon atoms of benzene, and when this residual affinity is almost entirely removed by the addition of an excess of hydrochloric acid the restraint is considerably reduced, and the vibrations become less restricted. The constitution of the three pyridones or hydroxypyridines was determined from their absorption in the following way. In the case of the α compound it was found that an alcoholic solution shows a well-marked band, and the addition of hydrochloric acid only shifts the band a little nearer to the ultra-violet without increasing its persistence. Furthermore, the addition of sodium ethylate does not shift the position of the band. The substance cannot therefore be phenolic in character; that is, it cannot have the formula



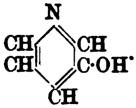
for if it had this constitution, sodium ethoxide would shift the band towards the red, as always happens with phenols; and further, since such a compound would be a true pyridine derivative, hydrochloric acid would increase the persistence of the absorption bands. Clearly, therefore, the formula must be



a conclusion which is confirmed by the close analogy of the absorption spectrum of N-methyl 2-pyridone—

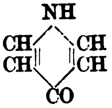


Exactly the converse is true in the case of the β-isomeride, for the absorption band of this compound is shifted towards the red by sodium ethoxide, and the effect of hydrochloric acid is very markedly to increase its persistence. The compound, therefore, must be phenolic, and a true pyridine derivative; that is, it has the formula



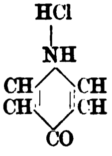
Moreover, the position of the absorption bands shows considerable analogy with those of phenol itself.

The γ-isomeride is peculiarly interesting, the compound showing an absorption band which is entirely removed by the addition of sodium ethoxide. This observation is analogous to the case of the aliphatic monoketones. The inference may be drawn from this that the substance is ketonic and has the formula



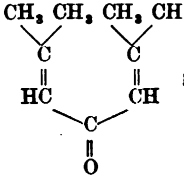
This is strikingly confirmed by the action of hydrochloric acid, which entirely alters the absorption, as may be seen from the full curve (Fig. 21), where the dotted curve is that of the γ-pyridone itself.

The hydrochloric acid should lock the compound in the form



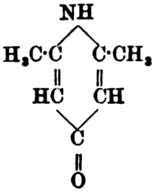
and as the CO group is between two ethylenic linkings a new absorption band should be produced.

It was found that phorone, in which this linking occurs

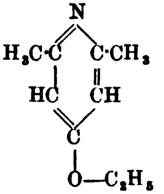


gives a very similar absorption. Clearly, therefore, the pyridone formula is confirmed.

Exactly similar conclusions are to be drawn from the absorption curves of γ-lutidone—

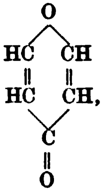


and here confirmatory evidence was forthcoming in the fact that γ-ethoxylutidine—

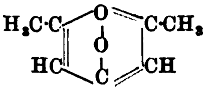


shows no absorption band, and therefore must have an entirely different composition from the parent lutidone.

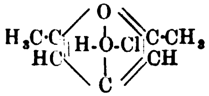
Somewhat similar arguments have to be applied to the elucidation of the constituents of the pyrones and certain applied compounds. It is well known that the pyrones do not form oximes or phenylhydrazones, and Collie pointed out that this fact could not be reconciled with the ordinary formula for the pyrones, for example,



and he suggested the bridged ring structure for dimethylpyrone—



The absorption curves of pyrone itself, dimethyl pyrone, and tetramethylpyrone show no absorption bands, but only a slight step-out, as is shown by the full curve in Fig. 22. The absorption curves of the hydrochloride do not even show this step-out, as can be seen from the dotted curve (Fig. 22). It is not possible to reconcile these observations with the ordinary formula, which contains a CO group between two ethylenic linkings, but they are just what would be expected from Collie's bridged formula, in which case the formula of the hydrochloride would be



and the step-out in the absorption curve of the dimethylpyrone itself may be traced to the residual affinity of the oxygen atom in the bridge, which is neutralised by the addition of the hydrochloric acid molecule. The addition of sodium ethoxide to the alcoholic solution of these bodies introduces a great change in the absorption, as can be seen from the dot-and-dash curve in Fig. 22, which is that of dimethylpyrone in the presence of 87 equivalents of sodium ethylate. This curve is very strikingly similar to that of γ-lutidone in the presence of hydrochloric acid, and as the chemical evidence shows

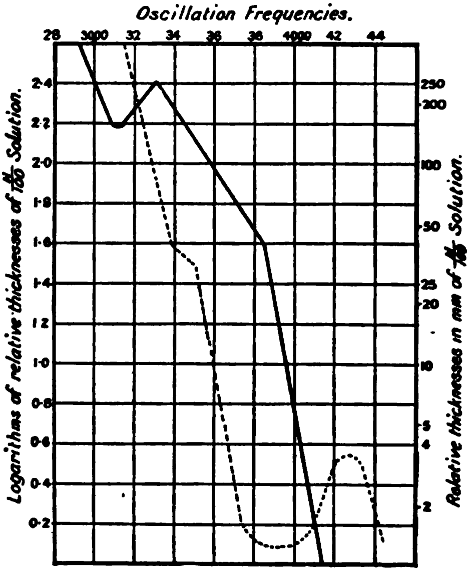


FIG. 21.

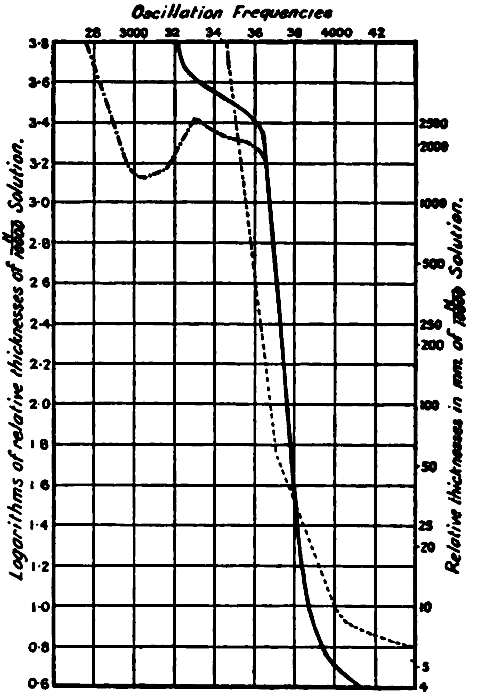
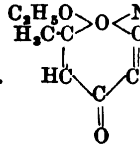


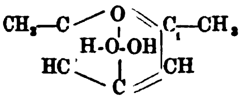
FIG. 22.

that an addition compound of dimethylpyrone and sodium ethoxide is formed, this suggests at once an analogous constitution for that compound, viz.

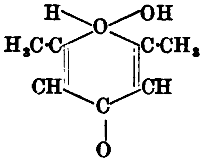


The addition of caustic soda to an aqueous solution of dimethylpyrone gives an entirely different absorption. It is well known that dimethylpyrone in aqueous caustic soda solution gives the sodium salt of diacetylacetone, and indeed the absorption curve of dimethylpyrone under these conditions approximates to that of diacetylacetone in aqueous alkali, so no doubt a considerable quantity of this substance is formed.

The determination of the constitution of diacetylacetone is complicated by the fact that the substance might have one of the following constitutions:—



1.

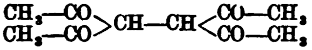


2.

$CH_3—CO—CH_2—CO—CH_2—CO—CH_3$

3.

and of these (1) is at once ruled out by the fact that diacetylacetone in no case shows an absorption resembling that of dimethylpyrone hydrochloride. In order to gain some idea of the absorption likely to be given by formula (3), tetracetylethane—



$$\begin{matrix}CH_3—CO\\CH_3—CO\end{matrix}\!>CH—CH<\!\begin{matrix}CO—CH_3\\CO—CH_3\end{matrix}$$

was examined in neutral and alkaline solutions. The constitution of this body is perfectly well known, and it was to be expected that its absorption will be analogous to the open chain form (3) of diacetylacetone. It was found that there was a strong similarity between the absorption of the diacetylacetone in water and tetracetylethane. The conclusion follows at once that in aqueous solution diacetylacetone exists in the open chain form.

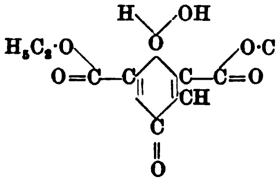
The alcoholic solution of diacetylacetone is different, for it exhibits a very broad absorption band. This band, however, extends over the regions occupied by the band of the open chain form of the substance and by the band of the sodium ethoxide compounds of the dimethylpyrones.

It may be concluded, therefore, that in alcoholic solution diacetylacetone exists as a mixture of the forms (2) and (3), and this conclusion is strengthened by the fact that the addition of sodium ethoxide to the alcoholic solution causes the broad band to be resolved into two bands, one of which is the same as that of the sodium ethoxide compound of dimethylpyrone and the other is that of diacetylacetone in aqueous alkali solution.

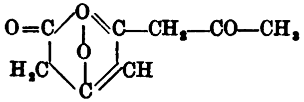
From similar arguments it was found that the colourless solution of ethyl xanthochelidonate in chloroform corresponds to the form—

$C_2H_5O\cdot OC—C(OH)=CH—CO—CH=C(OH)—COOC_2H_5$

whilst the yellow alcoholic solution contains also the closed form—

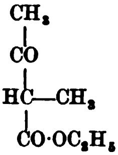


Finally, the results obtained in the examination of the absorption of dehydracetic acid and some closely allied substances would seem to argue that Collie's formula for this substance is the correct one, viz.—

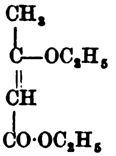


The simplest organic compounds at present known which exhibit selective absorption are the aliphatic ketones and allied compounds of the type of ethylacetoacetate and acetylacetone.

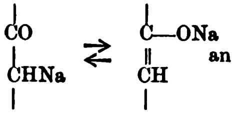
A few words may be said about these compounds, because the substitution of the hydrogen atom by the methyl group here induces a marked change in the absorption curves. A comparison of the absorption of ethyl acetoacetate with the well-known alkyl derivatives ethyl methylacetoacetate (I.) and ethyl β-ethoxycrotonate (II.)

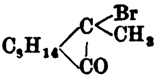


(I) and



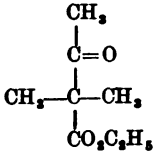
(II)

showed that the parent substance does not agree in its absorption with either of the two derivatives. Substances (I.) and (II.) do not show any absorption band in alcoholic solution, whilst ethylacetoacetate alone shows a tendency towards a band, and in presence of one or two equivalents of sodium ethoxide shows a well-marked band. From this it was concluded that ethylacetoacetate in alkaline solution is in a state of dynamic equilibrium, and that the absorption band is due to the reversible process  and also that the strongly marked band of acetylacetone in neutral solution is due to a similar process. Since that time investigations along two different lines have necessitated a slight modification in the above explanation of the absorption band. In the first place, it has been shown that all tautomeric changes of the above type are very much slower than is required by the above theory; and secondly, that absorption bands are shown, too, when such tautomeric equilibria are impossible, as, for example, in *αα′*-substituted camphor derivatives



$C_8H_{14}<\begin{matrix}C<\begin{matrix}Br\\CH_3\end{matrix}\\ |\\ CO\end{matrix}$

There is no doubt, however, that ethylacetoacetate can react either in the ketonic or the enolic form corresponding to I. or II. above, and also that there can be no doubt that the difference in the absorption of the body from that of the two fixed derivatives I. and II. is to be attributed to this cause, although it cannot be said that the absorption band is due actually to the dynamic equilibrium. Some recent and as yet unpublished experiments have shown that the compound I. and the still more rigidly ketonic substance



$$\begin{matrix} & CH_3 & \\ & | & \\ & C{=}O & \\ & | & \\ CH_3— & C & —CH_3 \\ & | & \\ & CO_2C_2H_5 & \end{matrix}$$

exhibit a well-marked band in presence of a great excess of sodium ethoxide, whilst the compound II. shows a band in presence of excess of acid. From this it is evident, were such evidence required, that the band cannot be due to tautomerism alone. It must originate in the mutual influence of the residual affinities of the alkali or acid upon I. or II., as the case may be. The extreme ease with which ethyl acetoacetate gives a band with alkali therefore must be connected with the ease with which this compound can pass from the ketonic into the enolic form and *vice versâ*.

Since acetylacetone gives an absorption band when dissolved in alcohol alone, it follows that the keto-enol change is even more easily brought about than in the case of ethyl acetoacetate. The absorption band in these compounds, then, is a measure of the amount that the closed systems are opened up by the influence of the solvent, and in certain respects may be considered as being analogous to that of the weak aromatic bases discussed above.

Although the absorption band is not due to the presence of a tautomeric equilibrium, yet the difference in the ease with which the absorption band can be developed forms a measure of the labile character of the hydrogen atom in the parent compound. For this reason, although a new explanation of the origin of the absorption band is introduced, it may readily be understood that spectroscopic results give a method of testing the presence of a labile or potentially labile hydrogen atom.

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E. C. C. B.

SPECULAR IRON ORE *v.* IRON; also HÆMATITE.

SPECULUM METAL. An alloy of 1 molecular proportion of tin and 4 of copper and a small quantity of arsenic, used for making the mirrors of reflecting telescopes.

SPEISS *v.* COBALT.

SPELTER *v.* ZINC.

SPERMACETI *v.* WAXES.

SPERMACETI, VEGETABLE, *Insect wax v.* WAXES.

SPERM OIL *v.* OILS, FIXED, AND FATS.

SPERMIN *v.* SYNTHETIC DRUGS.

SPERRYLITE. A mineral of interest as being the only naturally-occurring compound of platinum. It is the diarsenide $PtAs_2$, and forms minute, tin-white crystals, which are cubic with the same degree of symmetry as iron-pyrites (FeS_2). It was found in 1889 as a loose crystalline powder, filling small pockets in decomposed pyritic ore at the Vermillion gold mine in the Algoma district (22 miles west of Sudbury), Ontario. The platinum detected in small amounts (0·006–0·24 p.c.) in the pentlandite and nickeliferous pyrrhotite of Sudbury, Ontario, is perhaps present as sperrylite. A few minute crystals of sperrylite have been isolated from the platiniferous copper ore (covellite) of the Rambler mine in Medicine Bow Mountains, Wyoming. Other localities are in North Carolina and British Columbia, but the mineral is always of very sparing occurrence. The frequent presence of traces of platinum in sulphide ores of nickel and copper is, however, a promising indication for future discoveries (*v.* F. W. Clarke, Data of Geochemistry, Bull. U.S. Geol. Survey, No. 330, 1908, 610).

L. J. S.

SPESSARTITE *v.* GARNET.

SPHACELINIC ACID *v.* ERGOT OF RYE.

SPHÆROSIDERITE *v.* CHALYBITE.

SPHENE *v.* CALCIUM; also TITANIUM.

SPIEGEL-EISEN *v.* IRON.

SPIKENARD OIL (*Valeriana celtica* [Linn.]) is a thick yellow oil with an odour resembling that of valerian and hazelwort oils. It has sp.gr. 0·9693 at 20°; $[\alpha]_D - 42°$ saponification value 62·5; ester value (after saponification and acetylation), 71·9. It contains palmitic acid and a sesquiterpene, b.p. 255°, sp.gr. 0·9359 at 20°, $[\alpha]_D - 30·88°$ (J. Soc. Chem. Ind. 1909, 1272.

SPINACH, *Spinacia oleracia* (Linn.). Several varieties are known. The leaves are used as a vegetable.

Average composition (König)—

Water	Protein	Fat	Sugar	Other N-free extract	Fibre	Ash
89·2	2·7	0·5	0·1	3·5	0·9	2·0

About half the total nitrogen exists as real proteid, and the N-free extract includes about 0·9 p.c. of pentosans.

Spinach is remarkable for the high proportion of iron which it contains, largely in the form of organic compounds.

König gives, as the composition of the ash—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
16·6	35·3	11·9	6·4	3·4	10·2	6·9	4·5	6·3

Serger (Chem. Zentr. 1906, i. 1668) found that winter spinach contained from 86 to 89·5 p.c. of water, 9·5 to 13·3 p.c. of combustible matter, and 1·9 to 3·1 p.c. of ash. 100 grms. of the dry substance contained, on the average, 0·104 grm. of iron. From 100 grms. of fresh winter spinach, dilute alcohol extracted 4·3 grms. of substance which contained 0·179 p.c. of iron and gave 26·23 p.c. of ash, while the residual material yielded 8·7 grms. of dry substance containing 0·066 p.c. of iron, and gave 9·18 p.c. of ash. A considerable amount of the iron was also present in the matter extracted by a mixture of benzene, chloroform, and ether from the fresh leaves.

The amount of iron in spinach may be considerably increased by the addition of ferric oxide to the soil (Czadek, Chem. Zentr. 1904, i. 832).

For the great increase of crop resulting from the use of sodium nitrate and other artificial manures, *v.* Dyer and Shrivell, J. Roy. Hort. Soc. 1903, 27, part 4). H. I.

SPINEL (*Spinelle*, Fr.). A double oxide of magnesium and aluminium or a magnesium aluminate, $MgO{\cdot}Al_2O_3$ or $MgAl_2O_4$, crystallised in the cubic system. The name is also applied to a large isomorphous group of cubic minerals with the general formula $R''R_2'''O_4$, where $R''=Mg, Fe, Zn, Mn$, and $R'''=Al, Fe, Cr, Mn$. Other members of this group are magnetite, chromite, franklinite, gahnite (*qq.v.*). Spinel proper is of importance as a gem-stone. When red it is known as 'ruby-spinel,' 'spinel-ruby,' or 'balas-ruby,' and is often mistaken for the true ruby or corundum (*q.v.*), from which it is distinguished by its optically isotropic character, lack of pleochroism, and lower sp.gr. (3·6–3·7) and hardness (8). Large numbers of small, water-worn crystals are found in the gem-gravels of Ceylon. These are octahedral in form and often twinned on a face of the octahedron (hence the term spinel-twin for this type of twinning). Blue spinel ('sapphire-spinel') is much less common; stones of excellent quality have been made artificially (*v.* Gems, artificial). Spinel is much used for the jewelled pivot-supports of clocks and watches. L. J. S.

SPIRIT OF AMMONIA *v.* Ammonia.

SPIRIT OF HARTSHORN *v.* Ammonia.

SPIRIT OF SALT *v.* Hydrochloric acid.

SPIRIT OF WINE *v.* Alcohol.

SPIRIT VARNISHES *v.* Varnishes.

SPIROSAL. Trade name for the glycol ester of salicylic acid $OH{\cdot}C_6H_4{\cdot}CO{\cdot}OCH_2{\cdot}CH_2{\cdot}OH$. A colourless oily liquid, b.p. 169°–170°, at 12 mm. Soluble in water, alcohol, and ether, and readily miscible with oils (*v.* Salicylic acid and Synthetic drugs).

SPLENIN *v.* Synthetic drugs.

SPODUMENE (*Triphane*, Fr.). A member of the pyroxene group of minerals consisting of lithium and aluminium meta-silicate $LiAl(SiO_3)_2$, and crystallising in the monoclinic system. This formula requires 8·4 p.c. of lithia, but, owing to partial replacement by potash and soda, analyses show only about 5–7 p.c. The mineral is occasionally mined as a source of lithium salts. Sp.gr. 3·1–3·2, hardness 6½–7. The name 'spodumene' (from ***σποδούμενος***, something burned to ashes) has reference to the ash-grey colour shown by the common, opaque material. Transparent crystals are, however, colourless or often beautifully coloured, and are cut as gem-stones. These are strongly pleochroic, but they have the disadvantage of readily splitting, owing to the presence of a perfect prismatic cleavage. Clear yellow (rarely blue) fragments come from the gem-gravels of Brazil. Bright emerald-green crystals, coloured by a trace of chromic oxide, are found sparingly, together with beryl (emerald), in gneiss at Stony Point in Alexander Co., North Carolina; this highly-prized gem-variety is known as 'hiddenite' (or sometimes erroneously as 'lithia-emerald'). 'Kunzite' is another gem-variety of a delicate lilac or violet shade of colour, which has recently been found in the pegmatites at several places in San Diego and Riverside Counties in California and at Antsirabe in Madagascar. Large prismatic crystals of dull spodumene are well known from Huntington (formerly Norwich) in Massachusetts, whilst in the Etta tin mine at Harney Peak in the Black Hills of South Dakota enormous crystals, measuring as much as 42 ft. in length and with a cross-section of 3 by 6 ft., have been found; 37 tons of spodumene have been, it is said, mined from a single crystal (F. L. Hess and R. C. Wells, Amer. J. Sci. 1911, 31, 433). L. J. S.

SPRUCE OCHRE. *Brown ochre v.* Pigments.

SQUILL. (*Scilla*; *Scille*, Fr.; *Meerzwiebel*, Ger.)

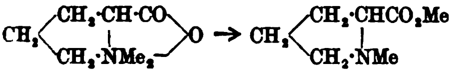
The fleshy bulb of *Urginea Scilla* (Steinheil), a liliaceous plant found on the shores of the Mediterranean (Bentl. a. Trim. 281). It has been employed in medicine from ancient times as a diuretic and expectorant. The bulb, already dried, is imported into this country mostly by way of Malta. Under the microscope the cells of its modified leaves are seen to be loaded with mucilage, in which numerous needle-shaped or square prismatic crystals of calcium oxalate are suspended (Flück. a. Hanb. 690).

The mucilage of squill contains a *gum*, which is precipitated by basic lead acetate, an *uncrystallisable sugar* (Flück. a. Hanb.) and *sinistrin* $C_6H_{10}O_5$ (Schmiedeberg, Zeitsch. physiol. Chem. 3, 112; Ber. 12, 704). The sinistrin of Schmiedeberg is probably a distinct substance from the constituent of dahlia root described under the same name by Marquart (Annalen, 10, 91). After removal of the gum from squill mucilage, by treatment with basic lead acetate, milk of lime is added, when an insoluble calcium compound is formed, from which free sinistrin may be liberated by carbonic acid. It is purified by successive solution in water and precipitation by alcohol. Sinistrin is a white amorphous powder, soluble in water, insoluble in alcohol, is lævorotatory (*cf.* Kühneman, Ber. 8, 387), and does not reduce Fehling's solution. Diastase is without effect upon it, but by boiling with dilute acid it is converted into lævulose and inactive glucose. The 'scillin' of Riche and Rémont (J. Pharm. Chim. [v.] 2, 291) appears to be nearly related to sinistrin.

By treating an alcoholic extract of squill with tannic acid, a compound is obtained containing the bitter and more active constituent of squill. This has not been satisfactorily isolated, although under the name of *scillitin* or *sculein* it has been much investigated. *See* further Mandet (Compt. rend. 51, 87), Schroff (Neues Rep. Pharm. 14, 241), Righini (Rep. Pharm. 63, 87), Tilloy (J. Pharm. Chim. 12, 635; [iii.] 23, 406), Vogel (Sitz. Ber. K. Akad. Wien. 6, 101), Lebourdais (Ann. Chim. Phys. [iii.] 24, 62), Marais (J. Pharm. Chim. [iii.] 30, 130), Landerer (Rep. Pharm. 47, 442). A bitter pulverulent compound, *scillain*, has, however, been obtained by Jarmersted, which, in its physiological action, resembles digitalin (J. 1879, 914). It is a glucoside, difficultly soluble in water but soluble in alcohol. The names 'scillipicrin,' 'scillotoxin,' and 'scillin' have been applied commercially to condensed pharmaceutical preparations of squill (Merck, Pharm. J. [iii.] 9, 1038). A. S.

STACHYDRINE $C_7H_{13}NO_2$. *Methyl betaïne of hygric acid*, or *dimethyl betaïne of a-proline*, is an alkaloid which was discovered by Planta and Schulze in 1890, in the tubers of *Stachys tuberifera* (Naudin) (Ber. 1893, 26, 939). It is also the chief basic constituent of the leaves of bitter orange (*Citrus Aurantium* [Linn.]) (Jahns, *ibid.* 1896, 29, 2065). It has been synthesised by converting ethyl hygrate into its methiodide and then treating the latter with silver oxide (Schulze and Trier, *ibid.* 1909, 42, 4654).

Stachydrine forms colourless, transparent crystals, which deliquesce in air and become opaque at 100° through loss of water of crystallisation. It melts at 210° and may be identified by its characteristic *aurichloride*, m.p. 225°, and by the fact that when heated in a glass tube, the vapours evolved turn a pine splint moistened with sulphuric acid, red (Schulze and Trier, Zeitsch. physiol. Chem. 1910, 67, 59). When heated with potash stachydrine evolves dimethylamine, and when distilled under reduced pressure it yields 66 p.c. of the isomeric dimethyl hygrate, thus—



$$CH_2\left\langle\begin{matrix}CH_2\cdot CH\cdot CO\\ |\\ CH_2\cdot NMe_2\end{matrix}\right\rangle O \rightarrow CH_2\left\langle\begin{matrix}CH_2\cdot CHCO_2Me\\ |\\ CH_2\cdot NMe\end{matrix}\right.$$

together with some trimethylamine and a little hygric acid (Trier, *ibid.* 324).

The *platinochloride* (in 3 forms), the *hydrochloride*, *sulphate*, *oxalate*, *picrate*, *nitrate*, and the *ethyl* derivatives have been prepared.

For further literature on the constitution and salts of stachydrine, *see* Planta and Schulze, Arch. Pharm. 231, 305; Engeland, *ibid.* 1909, 247, 463; Zeitsch. physiol. Chem. 1910, 67, 403; Schulze and Trier, *ibid.* 1909, 59, 233).

STACHYOSE, *Lupeose*, *v.* Carbohydrates.

STAGNIN *v.* Synthetic drugs.

STANNATES. Compounds of stannic oxide with bases (*v.* Tin).

STANNIC ACID *v.* Tin salts and oxides.

STANNITE or **Tin-Pyrites** (*Zinnkies*, Ger.). A sulphide of tin, copper, and iron, or a sulphostannate, Cu_2FeSnS_4, which has occasionally been found in sufficient amounts to be mined as an ore of tin (27·6 p.c. Sn). The iron is often partly replaced by an equivalent proportion of zinc (0–9 p.c.). Crystals are of rare occurrence; they are scalenohedral-tetragonal, with the same degree of symmetry and very nearly the same angles as copper-pyrites ($CuFeS_2$), but by twinning they give rise to pseudo-cubic forms. The crystallised material is iron-black with a bright metallic lustre (sp.gr. 4·45); but the massive mineral is usually yellowish or bronze-coloured (hence the miner's name bell-metal-ore), owing to an intimate intermixture with copper-pyrites. Stannite was formerly found in some quantity in several of the Cornish tin mines (*e.g.* Wheal Rock at St. Agnes; Carn Brea), and has also been mined at Borah Creek in New South Wales and Zeehan in Tasmania. Crystallised stannite has been found in some of the silver-tin mines of Bolivia (L. J. Spencer, Min. Mag. 1901, 13, 54). L. J. S.

STANNO-FLUORIDES *v.* Tin salts and oxides.

STAR ANISE, OIL OF, *v.* Oils, essential.

STAR SAPPHIRE *v.* Corundum.

STARCH (Lat. *Amylum*; Fr. *Amidon*, *Fécule*; Ger. *Stärke*, *Stärkemehl*, *Farina*).

1. *Occurrence.* In some form or other starch is one of the most widely-diffused substances in organic nature, occurring more or less abundantly in every plant that has, up to the present time, been examined. It is found in larger quantities in some families of plants than in others, and occurs in different parts in different plants; for instance, it is always found in great abundance in the seeds of all the cereals, as well as of the *Leguminosæ*, in the stems of various species of *Sagus* and *Cycas*, in the roots of many plants belonging to the family of *Euphorbiaceæ* and *Zingiberaceæ*, and in the tubers of the potato, canna, and cassava.

Starch is also found under varying conditions in different parts of the same plant; for instance, it is found in the green leaves of all plants during the daytime, the proportion varying according to the weather and time of day. It is generally present in greatest quantity towards the evening and least in the morning, whilst during the night the starch almost or completely disappears from the leaves, especially during the summer months. Starch is also found in the pith of trees and shrubs and in the various woody tissues; but its presence in these parts, as in the leaves, is not constant and equal, the same tissues at certain seasons being fully charged with starch and at others almost entirely devoid of it.

2. *Nomenclature.* In this country the term 'starch' appears to be applied generally to that obtained from all sources, with the name of the substance from which it is prepared usually prefixed to it, such as 'potato starch,' 'wheat starch,' 'rice starch.' In a few instances the affix starch is dropped, as in 'sago,' 'arrowroot,' or the product is known by some name given it in commerce, as 'tapioca,' 'tous-les-mois.'

In France the term 'fecula' (*fécule*) is applied to the starch obtained from roots and tubers, such as potato, manioc, arum; from stems, such as sago; and from fruits and seeds, as horsechestnut, acorns, &c.; whilst the starch obtained from all the cereals is defined as

TABLE I.—*Relative proportions of starch per cent. in various plants.*

—	Krocker	O'Sullivan
Wheat	53–56	54–55·5
Barley	38·6–37·9	46·2–46·4
Oats	27·9–36·9	35–38
Rye	45–47	44–46
Maize	66–67	54–58
Rice	—	75–77
Buckwheat	44	Krocker
Millet	53·7–55·5	,,
Haricot beans	37·7	,,
Peas	38·8	,,
Lentils	39·6–40	,,
Potatos (air-dried)	16–23	,,
Acorns	64·5	Gzubata
Pollen of common pine	7·1	Von Planta
Green bananas	12·1	Ricciardi
Soja bean under	5·0	Meissl & Böcker
Leaves of caoutchouc tree	5·4	—
Liquorice root	29·6	Sestini
Nasturtium officinale	2·9	Church
Tubers of yam	25·2	Moser
Dried pears	10·3	Bertram
,, apples	5·2	,,
Parsnips	1·0	Corenwinder
Kola nuts	33·7	Heckel & Schlagdenhauffen

amidon or starch. Most of these products are known in Germany as 'farina.'

3. *Physical characteristics.* To the naked eye pure starch presents the appearance of a white glistening friable powder, having a harsh feel when rubbed between the fingers, without taste or smell, is uncrystallisable, and undergoes no change under ordinary atmospheric conditions. Under the microscope it is seen to consist of granules of various forms—in most cases, however, more or less ovoid—and differing widely in size, form, and appearance, dependent on the source whence they are derived. According to Payen, they may vary in size from 0·002 mm. in diameter to 0·185 mm. These wide differences are the principal means by which the various kinds of starch may be differentiated one from another as they occur in commerce.

TABLE II.—*Diameters of the commoner varieties of starch granules.*

Starch from	Millimetre
Rhizomes of *Canna gigantea*	0·175
,, ,, *Maranta arundinácea* (arrowroot)	0·140
Tubers of potato	0·140
Broad beans	0·075
Sago	0·070
Lentils	0·067
Haricot beans	0·063
Peas	0·050
Wheat	0·050
Tubers of *Batata edulis*	0·045
Maize	0·030
Tapioca (*Jatropha manihot*)	0·028
Barley	0·025
Rice	0·022
Millet (*Panicum miliaceum*)	0·010
Buckwheat	0·009
Parsnip	0·007
Seeds of beetroot	0·004

It must be noted, however, that the size of the starch granules varies very considerably in different plants, being in some immeasurably minute, as in certain species of cactus; in others, as in the potato and tous-les-mois, attaining a comparatively large size, the several grains being readily visible with a simple lens.

In the same plant—and, indeed, often in the same cell—the size of the starch granules will be found to vary, being chiefly dependent on the relative age of the grains, so that when measures of starch grains from various sources are given they must be taken only to represent an average; but although the dimensions of the starch granules produced by any one species of plant are by no means constant, yet none of them depart very widely from this average, and so by reference to such a standard the starch granules of different plants may readily be differentiated microscopically one from the other by an expert.

4. *Formation of starch in the living plant.* Starch granules in the growing plant are formed in the homogeneous solid substance (protoplasm) of the chlorophyll corpuscles. They are at first visible as mere points, and gradually increase in size, so that eventually they may so completely fill up the space of the chlorophyll corpuscle that this may be represented by a mere covering film, and at last almost entirely disappear. These starch granules are sometimes extremely minute and very numerous, and so closely packed together as to fill the cell cavity, as in the case of rice and oat, whilst in other instances they are of much larger dimensions, so that only a comparatively small number of them are to be found in each cell.

Starch granules only grow and increase in size so long as they are in contact with the protoplasm and are exposed to light at a favourable temperature in the presence of carbon dioxide. Hence the formation of starch in the leaves of the growing plant must be regarded as a product of assimilation, and may be supposed to take place somewhat in the following manner. It is well known that carbohydrates can be oxidised to aldehydes, and arguing from this Baeyer suggested (Ber. 3, 63) that formaldehyde is the immediate product of assimilation, and by its condensation gives rise to the polymeric substance glucose—thus: $(CH_2O)_6=C_6H_{12}O_6$, and hence to the anhydride of it, starch. If this be the process which actually occurs in the plant, the function of chlorophyll is simply the decomposition of carbon dioxide into carbon monoxide and oxygen (Vines, Chem. Soc. Trans. 33, 375). That such is the case would appear from experiments recorded by Bokorny (Chem. Zentr. 1888, 858; 1891, 120), who found that algæ (*Spirogyra majuscula*), when placed in a culture solution containing 0·1 p.c. methylal, or 0·1 p.c. of sodium hydroxymethyl sulphonate, and 0·1 p.c. K_2HPO_4, and allowed to remain in air free from carbon dioxide and exposed to the light, contained, at the end of five days, very considerable quantities of starch, the sodium hydroxymethyl sulphonate being broken up into sodium sulphite and formaldehyde, which by condensation becomes converted into carbohydrate.

Brown and Morris (Chem. Soc. Trans. 1893, 623), in repeating experiments carried on by Bölim and A. Meyer, found that the chlorophyll granules not only form starch by the process of assimilation, but can also elaborate starch from nutritive solutions of certain sugars. It is difficult to imagine that a complex substance such as starch is the first product formed in the process of assimilation, and evidence goes to prove this. The rôle starch takes in the living plant is that of a reserve material, and the fact of its being of a colloidal nature gives weight to the fact. When required as nutriment for the plant it is rendered soluble by the agency of enzymes, *e.g. diastase*, and converted into readily diffusible sugars.

Under favourable conditions of assimilation the leaf cells are supplied with more than sufficient freshly assimilated materials in the form of sugars, and this excess of material is deposited as starch. The starch is only called upon when assimilation ceases. These authors concluded that cane sugar is probably the first sugar to be synthesised and may be regarded as the starting-point of all the metabolic changes taking place in the plant. It has the function in the first place of a temporary reserve material, and accumulates in the sap when the processes of assimilation are proceeding vigorously. When the degree of concentration reaches a certain limit starch commences to be elaborated by the chloroplasts, the starch forming a somewhat more stable and permanent reserve material than the cane sugar, which can be drawn upon when the more easily metabolised cane sugar has been partially used up.

The investigation of E. Fouard on the colloidal properties of starch (Compt. rend. 1907–1908, and Int. Cong. App. Chem. 1909) caused him to modify some of the views held by Brown and Morris on the functions of the living plant in respect of its starch. His examination of the mineral constituents of starch reveals the existence of mineral matters consisting chiefly of acid or basic phosphates, and in view of the action of acid and basic salts on the coagulation of the starch solution pointed out by A. Fernbach (Ann. Brass. et Dist., 1908, 11, 481–486), and of the fact that the vegetable cell contains a juice with variable reaction, it seems probable that the phosphatic impurity in the starch may play an important part in the changes of condition of the latter, and in its migrations within the vegetable organism.

He holds that the hypothesis that starch must be hydrolised to the condition of sugar before it can migrate is no longer necessary, since an opalescent pseudo-solution, when filtered through a collodion membrane, yields a clear filtrate containing starch in a state of perfect solution, which may be the form in which the migration of starch goes on in the plant.

5. *Structure of starch granules.* Starch granules, when examined under the microscope with a sufficiently high power, are found to consist of a series of distinctly stratified concentric layers, the outer ones being denser than those nearer the nucleus or hilum, which appears as a dark spot and generally occupies an eccentric position. This is well seen in potato starch. Occasionally two or more nuclei appear in one granule, and concentric layers may be observed surrounding each, as in the case of the haricot bean. The outer layer is the oldest in point of growth; the starch granule, according to Nägeli, increases in size from without inwards, so that each interior layer is younger and less compact than the one which immediately surrounds it; and since these layers are for the most part of variable thickness they cause the granule to deviate gradually in form from the originally spherical nucleus and assume a more or less ovoid form.

The investigations of R. Whymper (VII. Int. Cong. App. Chem. 1909) on the action of heat, mineral acids, and diastase, on the starch granule, support the theory of Nägeli. The fact that the small immature granules are not so easily attacked as the larger ones strengthens the view that the layers form internally during growth, the older ones expanding to make room for those newly formed, and consequently as the starch granules become larger, the outer layers become thinner and more easily penetrated by attacking agents.

Starch granules when intact are absolutely unacted on by cold water, and this was attributed, according to the earlier theories, to the presence of a protective coating of a different constitution to the other part of the granule. Water is absorbed to a very large extent by the interior contents of the granule, but none of the substance, which is to the highest degree colloidal, is able to diffuse into the surrounding medium.

If, however, the outer layer of the granule be ruptured by attrition, water is rapidly absorbed, the cell contents become swollen to a very great extent, and a small quantity of matter goes into solution. By treating the ruptured starch grains repeatedly with water, the whole of the cell contents may be removed, whilst the outer coating remains behind in the form of extremely thin layers; treated with a solution of iodine this outer coating gives a dirty yellow colour, whilst the cell contents are coloured an intense blue; this reaction, which is most characteristic of all starches, will be referred to again later on.

For many years the substance forming the outer layer of the starch granule has been known as starch cellulose, and the interior contents as granulose. They can be separated from each other in the following several ways: (*a*) by digesting the granules for several days with a saturated solution of sodium chloride containing 1 p.c. of hydrochloric acid, the cellulose remaining undissolved; (*b*) by digesting starch with saliva at 45°–55°, thus dissolving the granulose only; (*c*) by the action of certain schizomycetes which decompose the granulose of starch paste and leave the cellulose untouched; and (*d*) by the action of malt extract on starch paste in the cold (5–6 grms. starch per 100 c.c. water).

In the latter case limpidity is produced in a few minutes, the liquid is filtered, and the residue, which consists of starch cellulose, is washed well with cold water. Starch cellulose obtained in this way is perfectly insoluble in cold water, or in water heated up to 80°C.; it is not acted upon by diastase in the cold, nor up to 60°. By boiling with water it is converted to a great extent into soluble starch; a portion of it, however (about one-fifth), resists the repeated action of boiling water, but is readily dissolved in a dilute solution of potassium hydroxide, from which the greater portion of it can be re-precipitated by the addition of acetic acid. If, however, the alkaline solution be heated to boiling, the whole of the cellulose is slowly converted into soluble starch. Well-washed potato starch contains from 2 to 5 p.c. of cellulose. A considerable amount of attention has been directed to the structure of the starch granule, and the theory of Nägeli has been somewhat modified.

A. Mayer throws doubt on the existence of starch cellulose in the starch granule. He considers the granule to be homogeneous, for he points out that the delicate transparent skeletons left when the gelatinised granules are acted on by saliva, dilute acids, &c., are produced by the action of the reagent on the starch, and are identical with amylodextrin. The writers incline to the view that starch granulose differs from starch cellulose in being less dense in consequence of containing less water of hydration.

Maquenne and Roux (Ann. Chim. Phys. 1904, [viii.] 2, 109–135; 1906, [viii.] 9, 179–220) brought forward fresh views on the structure of the starch granule which would seem to be contrary to those of Nägeli and others that natural starches are a mixture of granulose and amylocellulose or starch cellulose, the latter being in a sense regarded as extraneous to the actual constituents of the starch granules. Maquenne and Roux stated that amylocellulose in different states of condensation forms the principal constituent of granules (about 80–85 p.c.) in admixture with another substance to which they asserted the viscosity of starch paste is due, and which they called amylopectin. This latter substance is of a mucilaginous nature, gives no colouration with iodine, and is dissolved, but only very slowly saccharified, by diastase, producing non-reducing sugars only.

Amylocellulose or amylose, as they prefer to call it, separates when starch paste or starch solution is allowed to stand. It is partly soluble in boiling water, and completely so in water at 150°; its solutions are devoid of gelatinising power, and give a blue colouration with iodine, being converted by diastase almost instantly and quantitatively into maltose. Amylocellulose can exist in a liquid form by heating under pressure to 150°–155°, or can be made to separate out, by cooling the concentrated solution, in granules resembling natural starch (reversion).

Fernbach and Wolff (J. Inst. Brew. 1904, 10, 216) showed that cereals contain an enzyme—amylo-coagulose—which causes a very rapid reversion of starch paste or solution to solid starch, having properties identical with amylose.

Z. Gatin-Gruzewska (Compt. rend. 1908, 146, 540–542) claimed to have separated amylopectin and stated that it forms the envelope of the starch granule, and consists of a series of sacs fitting one into the other, which are insoluble in cold water, but swell up in hot water, forming gelatinous pastes; it constitutes 40–45 p.c. of the starch.

Amylopectin gives an opalescent solution with alkali and water, which has an optical rotatory power of $[\alpha]_D$ +221°; the solution gives a purplish-blue colour with iodine, less intense than amylose.

Amylose dried to a fine powder partially dissolves in cold water, and entirely in hot water, giving opalescent solutions which give a clear blue colour with iodine; it dissolves rapidly in the presence of small quantities of alkali, and has an optical rotatory power in such solution $[\alpha]_D$+184·4°.

Maquenne (Compt. rend. 1908, 146, 542) states that the amylopectin isolated by Gatin-Gruzewska was impure and still contained amylose insoluble in boiling water. He holds the view that amylopectin and amylose cannot be regarded as homogeneous, but must consist of a complex mixture of homologous or differently condensed products. There is a likelihood that in the natural formation of the starch granule the amylopectin is derived from amylose by condensation just as amylose is derived from sugars. This gradual transition would explain the difficulty of separating these two substances, as there appears to be no sharp transition between the group of slightly soluble amyloses occupying the end of the series, and that of the least resistant amylopectins.

A. Fernbach (Ann. Brass. et Dist. 1908, 11, 481) is of opinion that solid starch should be regarded as a coagulated substance, which in nature has probably passed from the state of apparent solution to the solid form, and all the changes that starch can undergo without chemical alteration should be regarded as changes of this or the opposite kind. The conversion of solid starch into starch-paste or with so-called soluble starch is, in a sense, a change of the latter kind; the partial reversion of starch-paste to a solid substance is a change of the former kind. Attention is drawn to the fact that natural starches, like malt extract, are acid to phenolphthalein and alkaline to methyl orange, and he considers that the properties of starch depend almost exclusively on the nature and proportion of the accompanying mineral substances. These conclusions are based on the results of his investigation on amylo-coagulose, the enzyme present in cereals which coagulates starch-paste, which he found to have a maximum activity in a medium which is neutral to phenolphthalein.

Under polarised light starch assumes a most characteristic appearance. When examined under crossed Nicol prisms the field remains dark, but each granule assumes a glistening grey appearance, as if self-luminous, and is marked with a black cross. If, then, the object be slowly rotated in the field of view, the cross will remain fixed with regard to the field, one pair of its arms being parallel to the principal plane of the polariser, and the other parallel to the principal plane of the analyser. If next the object be allowed to remain stationary, and the polariser or analyser be rotated, the cross will rotate with it, but with only half the angular velocity; if, next, a thin plate of selenite be introduced between the polariser and the object, and whilst the Nicols are crossed, most beautiful chromatic effects may be obtained.

6. *Chemical properties.* Starch is absolutely insoluble in cold water, alcohol, ether, or any other known solvent.

Ordinary air-dried starch usually contains about 18 p.c. of water, which may be entirely driven off by heating for some time in a current of dry air at a temperature of 100°–105°. Under this condition starch appears to be a most highly hygroscopic substance, which rapidly absorbs moisture from the air until it regains its original 18 p.c.; if exposed to a damp atmosphere it is capable of absorbing as much as 35 p.c. of moisture.

The specific gravity of air-dried starches varies considerably, the variation being mostly due to the moisture content. Starches that have been freed from water have not absolutely the same specific gravity, anhydrous potato having a value 1·650, and anhydrous arrowroot 1·5648.

7. *Action of heat.* Freed completely from moisture, starch may be heated to a temperature of 160° without undergoing any change; at temperatures higher than this it becomes coloured, and is partly converted into dextrin. If, however, ordinary air-dried starch be heated to 160° it quickly undergoes decomposition, becoming converted to a greater or less extent into dextrin and reducing sugars, the action varying with the particular kind of starch used (*v.* DEXTRINS).

Experiments were made by the writers as to the effects of heat on different varieties of starch. Potato, sago, and rice were heated to 190° for two hours, cooled down, dissolved in cold water, and the specific rotatory powers of the solutions taken. Potato and sago starch were entirely decomposed under these conditions, and their solutions showed a specific rotatory power of $\alpha_D = 154{\cdot}3$ for potato, and $\alpha_D = 193{\cdot}3$ for sago; rice starch appears to offer great resistance to the action of heat, being only partially decomposed at the above temperature.

According to Schubert (Monatsh. 1884, 472), the starch granule, under the influence of high temperature, is altered in such a manner that those layers which are rich in granulose are at once converted into soluble starch and dextrin, whilst the principal portion of the layers rich in cellulose only undergo this transformation after a time. When starch which has been subjected to a high temperature is treated with cold water, the soluble starch, dextrin, and other products of decomposition go into solution, and an organised residuum is left, which resembles the form and structure of the original granule, and contains small quantities of unchanged granulose.

By dry distillation starch yields carbon dioxide, gaseous hydrocarbons, water, acetic acid, and empyreumatic oil, and leaves a porous cinder.

On distilling dry starch with lime in the proportion of 1 to 4 it yields acetone, mesityl oxide, a series of ketones, and various condensation products of acetone (Horvat, Chem. Zentr. 1887, 38).

By distillation with manganese dioxide and dilute sulphuric acid it yields carbon dioxide, aqueous formic acid, and furfural.

In the open fire it softens, swells up, evolves choking vapours, and finally burns with a bright flame.

Distilled with hydrochloric acid and manganese peroxide, it yields, among other products, trichlorinated acetic aldehyde and pentachlorinated propionic aldehyde.

8. *Action of hot water.* When starch is brought into contact with hot water the contents of the granules, owing to a large absorption of water, swell up enormously; and, at a temperature varying according to the variety of starch, ultimately rupture the outer layer, forming a viscous liquid which is known as 'starch paste.'

The different varieties of starch gelatinise with hot water at very different temperatures, as is seen in the following table by Lintner (Brauer und Malzer Kalendar, 1889), which gives the temperatures of complete gelatinisation for the commoner varieties of starch:—

TABLE III.

Starch from	Temperature at which complete gelatinisation takes place
Potato	65°C.
Maize	75°C.
Barley	80°C.
Wheat	80°C.
Rye	80°C.
Rice	80°C.
Kilned malt	80°C.
Green malt	85°C.
Oat	85°C.

This table gives the temperatures at which the various starches gelatinise completely in the pure state. In the crude condition a much higher temperature is necessary.

Under the action of boiling water the starch granules do not all swell up and burst at once—the younger ones being attacked first, the older last. This progressive action of heat can be very well observed when potato starch has been suspended in 12–15 times its weight of water, and gradually heated on the water-bath; hardly any change is apparent up to 55°, at 57° the younger granules begin to show signs of rupture, and as the temperature rises this process of swelling and bursting of the contents through the outer wall of the granule goes on increasing, the earliest-formed granules being the last to give way, until, at a temperature between 65°–70°, a thick viscous liquid, of uniform consistency, is obtained.

According to Bruckner (Monatsh. 4, 889), starch paste and granulose are identical, and no sharp distinction can be drawn between swollen starch granules and starch paste; thus at 46° potato starch swells distinctly, at 59° it begins to lose its form, and at 62·5° it is converted into a paste and shows no trace of its original form.

On cooling, starch paste contracts and becomes, when very thick, a firm solid mass, which, after standing a short time, cracks; its maximum contraction is reached at the freezing-point, when a separation of the water and starch takes place to a certain extent. Upon raising the temperature, the water which had been frozen out does not again combine with the starch, and may be drained away, whilst the consolidated starch paste remains as a felty mass which, when dry, has the appearance of mother-of-pearl (Payen).

Wide differences in the viscosity of this paste are observed, depending not only upon the variety of starch employed, but also upon the treatment to which the starch is subjected during the processes of purification and drying.

According to Brown and Heron (Chem. Soc. Trans. 35, 596), starch which has been treated with dilute potash and acid in the process of purification produces a paste of less viscosity than the same starch which has not been so treated; they also find that great variations in the consistency of the resulting paste are produced by slightly altering the manner of drying.

These facts are of importance, seeing that the technical value of a starch in certain industries depends entirely upon the viscosity produced by it when acted upon by boiling water.

Potato starch is used in large quantities for sizing and stiffening yarn and cloth, so that it is of importance to the manufacturer to obtain that sample of starch which will make the stiffest cloth and which has the greatest tenacity. In order to determine this, the following method has been recommended by O. Soare and P. Martens (Zeits. Spiritusind, 1903, 26, 436–437). An immersion body is constructed of a circular brass plate, 22 mm. in diameter, to which a brass wire is fixed vertically at the centre, having a mark at a distance of 3 cm. above the disc, and terminated by a hook at the top. The starch paste is prepared by weighing out 7 grms. of starch into a beaker of 200 c.c. capacity provided with a small metal spoon. The whole is tared, and 164 c.c. of boiling water are added with continuous and gentle stirring all the time. This may be effected either immediately or after immersion in a boiling water-bath for 2, 5, or 10 minutes. This spoon is then removed and the brass disc supported by a clamp is immersed in the paste exactly up to the mark; 10 c.c. of olive oil are poured over the surface to prevent the formation of a hard skin by evaporation, and the whole is left at rest for 20 hours at a temperature of about 17·5°. A hand balance, one of the pans of which has been replaced by a counterpoise, is attached to that of the disc. On the other scale pan an uninterrupted stream of sand is discharged at a uniform rate of about 9 grms. a minute, until the disc is torn from the paste. The weight of the sand is then taken as a measure of the stiffness of the paste. Experiments showed that the time during which the paste was heated at the boiling-point had a considerable influence on the results. Certain starches, especially those with a high gelatinising-point, such as wheat and maize starches, did not attain their maximum stiffness until they had been boiled for several minutes; on the other hand, certain potato starch pastes had a maximum stiffness without heating, any heating beyond that necessary to produce the maximum stiffness, caused a rapid decrease in stiffness. The values of the various samples showed a tendency towards equalisation by prolonged heating.

H. Cappenberg (Chem. Zeit. 1910, 34, 218–220) has designed a viscosimeter for starch pastes in which a spherical weight of standard dimensions is drawn upwards through a column of the paste of fixed height and temperature, the time occupied in doing this, under the pull of a known load in grams, being noted. A series of trials are made with a regularly decreased load, these being tabulated for comparison, as single observations with a fixed load are useless for this purpose. In comparing starches it was found that pastes containing 5 p.c. of potato starch and 9 p.c. of wheat starch gave coincident figures, and it may reasonably be assumed that for these samples the thickening powers were in that ratio.

Erwen (J. Soc. Chem. Ind. 1907, 26, 501–502) makes solutions in the cold with the help of sodium hydroxide, and determines their viscosities in a Redwood viscosimeter. The weighed sample of starch is shaken continuously with 230 c.c. of cold water, and 15 c.c. of a 10 p.c. solution of sodium hydroxide with the addition of enough water to bring the whole up to 250 c.c., until the solution begins to thicken. It is allowed to stand until the next morning before measurement. When close attention is paid to constancy of procedure the method is claimed to give concordant results with the same starch, whilst different starches and different brands of the same starch are easily differentiated.

As has already been stated, starch paste is composed of granulose or amylose, which exists in a state of partial solution, and starch cellulose or amylopectin, a mucilaginous substance to which the viscosity of the paste is due. The sp.gr. of starch paste, as determined by Brown and Heron, is 1·66 at 15·5°. It is one of the most perfect colloids known, as, since its solution-molecule is extremely large, its passage through the fine pores of filter-paper is very difficult. It rotates a ray of polarised light strongly to the right, but owing to the want of transparency in the liquid, the determination of its specific rotatory power is exceedingly difficult, it being impossible to obtain good observations with solutions of even very pure starch containing more than 1 grm. of substance per 100 c.c. The mean of Brown and Heron's observations from solutions of this strength give $\alpha_j=208°$, but it is possible that this number is too high, owing probably to the presence of a small portion of soluble starch, which evidently possesses a higher rotation, for the above authorities state that if a dilute solution of starch paste (1 grm. per 100 c.c.) be boiled for 30 minutes the liquid becomes more transparent, and at the same time an increase in the rotation is observed.

9. *Soluble starch.* Under certain conditions starch undergoes a peculiar modification, by which it is rendered completely soluble in water from which it can be precipitated as a brilliant white flocculent substance by alcohol, or if the solution be somewhat concentrated and allowed to stand some time a white granular precipitate slowly separates out. Under these conditions, the precipitate is always found by microscopic observation to be made up of minute particles, entirely without structure and without action on polarised light. Lintner found, however, that when a dilute solution is submitted to a low temperature, it is possible to obtain this precipitate in the form of sphærocrystals.

Although but sparingly soluble in cold water (not more than 2 or 3 grms. per 100 c.c. ever going into solution), it readily dissolves in water at 60°–70°, and separates out again on cooling as a white flocculent amorphous precipitate. To this substance has been given the name 'soluble starch.'

When washed with alcohol and dried the precipitated starch becomes very friable, but after once being dried is almost completely insoluble in water.

When starch paste is largely diluted with water and boiled for some considerable time, a portion of it goes into solution and may be easily filtered off. A similar reaction may be brought about more rapidly if starch with about ten times its weight of water be heated under pressure up to 130°–150° (Stumpf, Bied. Zentr. 1880, 457). Under these conditions the greater portion of the starch is rendered soluble, and corresponds to the solutions of Maquenne and Roux's so-called amylose which enters into solutions at this temperature.

The same effect may be brought about by treating potato starch with a 5–10 p.c. solution of hydrochloric acid for 7–10 days (Lintner, J. pr. Chem. 1886, 34, 378); the starch granules are then washed until free from acid, and on treating with boiling water, dissolve completely without the production of the usual viscid paste. This extraordinary change in the properties of the granules is not accompanied by the slightest change of structure, and the altered granules have the same appearance under the microscope and the same influence on polarised light as the unaltered starch.

Soluble starch may be prepared, according to O'Sullivan, as follows: Starch paste is acted on with the least possible quantity of the cold water extract of malt, previously heated to 75° for 30 minutes, or with diastase solution, or with dilute sulphuric acid (sp.gr. 1·120) at 75°, and further action stopped as soon as limpidity is produced by raising the liquid quickly to the boiling-point if diastase or malt extract be employed, or by adding barium carbonate if sulphuric acid has been used, until neutrality is produced. The liquid is then filtered and evaporated until a slight skin begins to form on the surface; when the soluble starch falls out on cooling as a brilliant white precipitate. This is allowed to rest for a few days, and then treated with cold water, with which it is washed well upon a filter. It is purified by dissolving it in as small a quantity of boiling water as possible, and again filtering, if necessary using a hot-water funnel. On cooling, the soluble starch separates from the filtrate as before.

Perhaps the readiest way of preparing soluble starch is that recommended by Zulkowski (Chem. Zentr. 1888, 1060), who finds that starch dissolves in hot glycerol and is converted into the soluble modification; this, in turn, if the action be continued, becoming transformed into erythrodextrin and achroodextrin, with the production at the same time of reducing sugars. 60 grms. of dry-potato starch are heated for half an hour with 1 kilo. of glycerol at a temperature of 190°, then cooled down to 120°, and the soluble starch precipitated by the addition of two or three times its volume of strong alcohol. If necessary, the precipitate may be further purified by dissolving again in the smallest possible quantity of boiling water, and reprecipitating therefrom with 90 p.c. alcohol.

Soluble starch has been prepared by treating starch granules with a 1 p.c. solution of caustic soda (Wroblewski, Ber. 1897, 30, 2108); and Syniewski has also prepared it by treating potato starch suspended in water with sodium peroxide (*ibid.* 1897, 30, 2415). This product is soluble in cold water up to 12·5 p.c., and dissolves in hot water in any proportion. Soluble starch prepared in this way, however, appears to be quite distinct from that prepared according to Lintner's method.

Pure soluble starch prepared by the methods of Lintner and O'Sullivan, when in solution, rotates a ray of polarised light strongly to the right. Brown and Morris find its specific rotatory power to be $[\alpha]_{j3\cdot86}+216°$, $[\alpha]_{D3\cdot86}+195°$. Lintner gives it as $[\alpha]_D+200°$, and Brown, Morris, and Millar give a value in 2·5–4·5 p.c. solutions at 15·5° of $[\alpha]_D+202°$.

E. Fouard has carried out some interesting investigations with regard to starch solutions and soluble starch, but space does not permit any further description (*cf.* Compt. rend. 1908–1909; Seventh Internat. Cong. App. Chem. 1909).

Soluble starch has no action whatever on Fehling's solution, and, like starch paste, its solution is coloured an intense blue with iodine.

10. *Action of alkalis.* When a moderately-strong solution of potassium or sodium hydroxide is added to starch paste, the previously opalescent liquid is rendered perfectly transparent without any alteration taking place in its viscosity. This increase in transparency is due to the solution of the suspended starch cellulose by the alkali. The specific rotatory power is at the same time considerably lowered, but resumes its original value if the alkali be neutralised by acetic acid. These facts point to the production of a definite compound of starch with potash or soda. An interesting feature in this reaction is that, after acidification, the solution remains transparent, and possesses all or nearly all the viscosity of the original starch paste (Pfeiffer and Tollens, Annalen, 1882, 210, 285; Brown and Heron, Chem. Soc. Trans. 35, 596).

When starch is treated with an alkaline

solution the granules swell up and form an exceedingly tough viscous mass, which readily dissolves in water, forming a solution in no way differing from that produced by the action of alkali on starch paste.

Symons (Pharm. J. [iii.] 13, 237) has investigated the process of swelling of starch granules under the action of heat at different temperatures, and of alkaline solutions of varying strengths, and concludes that the process of swelling through the action of these widely-differing agents is one and the same, and, as a result of his experiments, proposes a method whereby the several varieties of starch may be detected by their behaviour with dilute alkaline solutions of definite strength.

The most suitable are solutions of caustic soda of 0·5–1·5 p.c. 0·1 grm. of the starch is repeatedly stirred up with 1 c.c. of the particular soda solution, and, after 10 minutes, examined under the microscope.

Ammonia solution, either dilute or concentrated, has no action whatever on starch or on starch paste.

If a trace of starch be added to a solution of a salt of ammonia, and then a solution of sodium hydroxide drop by drop, the starch remains unchanged until the whole of the ammonia salt has been decomposed; but the least excess of soda causes immediately an expansion of the starch granules.

Tables IV. and V. give the results of Symon's experiments for various starches.

TABLE IV.—*Action of heat on starch granules.*

Variety of starch	Order of relative size of granules	Few granules swollen at	Majority of granules swollen at	All granules swollen at
		°C.	°C.	°C.
Potato .	2	55	60	65
Cassava .	7	58	63	68
Natal .	4	58	65	70
Wheat .	5	60	65	70
Tous-les-mois	1	65	68	72
Bermuda .	4	62	69	73
Sago . .	3	64	68	74
Maize .	6	65	70	77
Oat . .	8	65	70	77
St. Vincent	4	66	73	77
Rice . .	9	70	75	80

Starch exhibits a peculiar reaction with ammoniacal copper solution. Dry starch readily absorbs cupric oxide from ammonio-cupric oxide solution, and decolorises the liquid, the action being more rapid if the starch has previously been slightly moistened. Starch paste acts in a similar manner. A deep-blue compound is formed, from which water, and even dilute ammonia, remove only traces of copper. Repeated washing, however, with strong ammonia eventually removes every trace of copper (Guignet, Compt. rend. 109, 528).

Dilute hydrochloric acid immediately decomposes this compound, forming cupric chloride, which may be readily removed by washing with water, leaving the starch granules intact.

After prolonged digestion with strong ammonia in the cold, the granules swell up and become converted into the soluble modification.

TABLE V.—*Action of dilute NaHO on starch granules.*

Variety of starch	Order of relative size of granules	Few granules swollen with	Majority of granules swollen with	All granules swollen with
		p.c.NaHO	p.c.NaHO	p.c.NaHO
Potato .	2	0·6	0·7	0·8
Oat . .	8	0·6	0·8	1·0
Natal .	4	0·7	0·8	1·0
Tous-les-mois	1	0·7	0·9	1·0
Wheat .	5	0·7	0·9	1·0
Bermuda .	4	0·8	0·9	1·1
Sago . .	3	0·8	0·9	1·1
Maize .	6	0·8	1·0	1·1
Cassava .	7	0·8	1·0	1·1
St. Vincent	4	0·9	1·0	1·2
Rice . .	9	1·0	1·0	1·3

On heating the compound of cupric oxide and starch with water at 80° the starch gelatinises, forming with the cupric oxide a beautiful blue viscous liquid.

Starch possesses the property of combining with other bases than sodium and potassium. If to the transparent colourless jelly formed by acting on starch with sodium hydroxide, a 7 p.c. aqueous solution of calcium chloride be added, double decomposition takes place, and a thick, white, insoluble mass is formed, which is a compound of starch with calcium. A series of compounds of starch with other bases may similarly be formed, in which the starch cannot be detected by means of iodine. The starch in such compounds is, however, immediately set free by acids (Payen).

Starch is completely precipitated from a dilute aqueous solution by a solution of lime in sugar-syrup. The composition of the precipitate varies according to the quantity of lime added. With baryta and strontia water similar compounds are formed (C. J. Lintner, Zeitsch. angew. Chem. 1888, 232).

11. *Action of acids.* A swelling of the starch granules, similar to that occasioned by sodium or potassium hydroxide, is produced immediately by all mineral acids, and by some organic acids, *e.g.* tartaric and citric acids, after being in contact for some time. No swelling is produced by acetic or oxalic acids, no matter how concentrated their solutions may be.

When air-dried starch is triturated with concentrated sulphuric acid considerable heat is evolved, and, after a short time, complete carbonisation takes place. If, however, the starch be previously freed from moisture, on addition of the acid the granules swell up and form certain mucilaginous compounds of the general formula $C_{6n}H_{10m}O_{5n-x}(SO_4)_x$, which are soluble in water, and rotate a ray of polarised light strongly to the right. When boiled with alcohol they lose all the sulphuric acid, leaving a modified form of starch. Upon neutralising the aqueous solution with bases, uncrystallisable salts are formed (Hönig and Schubert, Monatsh. 6, 768).

When diluted sulphuric acid 1 : 2 to 1 : 4 is added to air-dried starch, a swelling up of the granules takes place, and the mass becomes thick and viscous. On standing some hours the viscosity disappears, the iodine reaction showing the presence of soluble starch only; but on standing for some days this becomes gradually hydrated to maltose, and finally to dextrose.

Nitric acid yields with starch various products, depending on the strength of the acid, temperature, and duration of the action.

When starch is boiled for some time with moderately concentrated nitric acid (sp.gr. 1·200) it is completely converted into oxalic acid. Cold concentrated nitric acid (sp.gr. 1·520) added to starch causes the granules to swell up, first into a viscous mass, which after a short interval becomes quite limpid; if now water be added to this solution, according to Braconnot (Annalen, 7, 245), a white powder is precipitated which when dry explodes upon being struck. This substance has been termed *xyloïdin*, and has the same composition as the corresponding compound of cellulose.

If, however, the solution of starch in nitric acid be allowed to stand, water precipitates less and less of xyloïdin, and at last none, whilst a substance resembling saccharic acid remains in solution (Pelouze, Compt. rend. 7, 713).

When starch is heated with a mixture of nitric acid and fuming sulphuric acid containing some 2–3 p.c. of free SO_3 at a temperature of 45°–50° a starch nitrate having a formula $C_{12}H_{12}(NO_2)_8O_{10}$, and containing about 16·5 p.c. of nitrogen, is formed. It is an orange-coloured highly explosive powder, and is soluble in ether-alcohol.

Strong hydrochloric acid added to dry starch causes the granules to swell, and in a very short time to become a thick, semi-translucent, viscous mass. If to this a large quantity of cold water be added, a milky fluid results, which consists entirely of the soluble modification. If, however, the swollen mass be allowed to remain for a few days, the soluble starch will be found to have entirely disappeared, whilst at the same time the viscous mass becomes perfectly limpid, and separates into two layers, the lower one consisting of the products of decomposition of the granulose—namely, achroodextrin, maltose, and dextrose—whilst the upper layer consists exclusively of starch cellulose.

If, however, the action of very dilute (1–2 p.c.) mineral acids, such as sulphuric or hydrochloric, upon ungelatinised starch in the cold be allowed to continue for some considerable time (two months or more), the granules gradually become disintegrated, a portion becoming converted into dextrose and going into solution, whilst the residual substance retains little or nothing of the original form of the starch granule. Concurrently with these changes, the iodine reaction undergoes considerable modification, the original deep-blue colour gradually giving place to purple, and this, through reddish-purple and reddish-brown, to a pale yellowish-red, which is not further modified, even if the starch remain in contact with the acid for some years. This residual substance, after being washed with cold water until free from acid, is completely soluble in hot water, from which it may be precipitated by alcohol in the form of a brilliant white powder, which is highly crystalline in appearance when the precipitation has taken place slowly. This, under the microscope, is seen to consist of sphæro-crystals made up of thin needles or plates arranged radially, and so closely resembling the sphæro-crystals of inulin that the two substances cannot be distinguished by microscopical examination alone. This substance has been termed amylodextrin by Nägeli. It gives an intense reddish-brown colouration with iodine (Brown and Morris, Chem. Soc. Trans. 55, 449).

The further action of acids on starch differs very considerably according to the degree of concentration, temperature, and pressure.

When starch is heated to boiling with very dilute acids (2 p.c.), little or no formation of paste takes place, the starch being rapidly converted first into soluble starch, then into dextrin and maltose, and, if the action be sufficiently prolonged, finally into dextrose. If this action be stopped at various stages by neutralising the acid with calcium or barium hydroxide, and the filtrates examined at a very early period, the liquid will be found to consist almost entirely of a solution of soluble starch. Later on, this disappears, giving rise to dextrin and maltose; and, according to Brown, Morris, and Moritz (Eng. Pat. 19003, 1889), to a series of intermediate bodies known as maltodextrins. A little later, dextrose makes its appearance, and this continues to increase at the expense of the maltose already formed, the dextrins and maltodextrins being successively hydrated to this body, until finally dextrose only is found in solution. If, however, the action be carried to this extreme point, the dextrose in its turn is acted upon by the acid, giving rise to condensation products, caramel, and other humous substances (Valentin, Jour. Soc. Arts, 24, 404; Scheibler and Mittelmeier, Ber. 23, 3060).

At temperatures higher than 100°, or under pressure, the above changes take place very rapidly. Tables VI. and VII. give some idea of these relative changes.

12. *Action of chlorine, bromine, and iodine.* Chlorine gas has no action on starch granules either in the dry state or when moistened with water, but when passed through thin starch paste for some hours the viscosity disappears, the greater portion of the granulose becoming converted into soluble starch and erythrodextrin; this action takes place slowly in the cold, but quickly at a high temperature.

Bromine colours starch granules yellow, but does not seem to form any definite compound, as the yellow colour disappears on repeatedly washing the granules with water.

Very little action is produced on starch paste by bromine in the cold, but if heated on the water-bath for some time the starch paste is liquefied and converted into the soluble form.

The most characteristic reaction for starch, wherever it occurs, is the production of a deep-blue colouration with a solution of iodine. This colouration is imparted by the iodine to the granulose in the intact starch granules as well as when in the condition of starch paste and of soluble starch. This iodine reaction was discovered as far back as the year 1813 by

Table VI.—*Action of sulphuric acid (dilute) on starch at different temperatures.*

Time	Colour of solution	Iodine reaction	$[\alpha]_{D3\cdot86}$	$K_{3\cdot86}$
Series A.—2 p.c. acid. Temperature, 150°C.				
30 secs.	None	Full brown, trace of starch	142·2	42·3
2 mins.	None	Brown	87·2	62·2
5 ,,	Slight	None	61·7	89·1
10 ,,	Much	—	56·8	81·2
30 ,,	—	—	54·3	71·6
Series A.—2 p.c. acid. Temperature, 125°C.				
2 mins.	None	Blue	All soluble starch	
5 ,,	None	Brownish-violet	163·0	29·2
10 ,,	None	Brown	128·6	55·4
Series B.—1 p.c. acid. Temperature, 150°C.				
30 secs.	None	Full brown	152·6	32·2
3 mins.	None	None	83·5	59·6
5 ,,	Light-straw	—	61·1	78·7
Series B.—1 p.c. acid. Temperature, 125°C.				
10 mins.	None	—	153·4	34·3
20 ,,	None	—	118·5	55·6
30 ,,	None	—	97·2	69·7

Table VII.—*Action of various acids on starch at* 150°C.

Acid	Time	$[\alpha]_{D3\cdot86}$	$K_{3\cdot86}$
0·25 p.c. Sulphuric .	10 mins.	138·9	38·2
0·25 ,, Hydrochloric	10 ,,	60·6	84·1
2 p.c. Phosphoric .	10 ,,	117·8	55·1
1 ,, Tartaric . .	20 ,,	170·3	24·6
1 ,, Oxalic . .	10 ,,	94·4	76·5
1 ,, Acetic . .	30 ,,	No action	

Stromeyer, and has been the subject of much investigation since then.

When an aqueous solution of iodine is added to starch paste an intense deep indigo-blue colouration is produced. This blue colouration—which is a most characteristic test for starch, not being produced by any other known body—is due to the formation of a definite chemical compound, or probably more than one compound, of iodine and starch granulose, and is provisionally termed iodide of starch.

It is best prepared by adding an excess of iodine to a thin solution of starch; iodide of starch then separates out as a blackish-violet powder, which, when washed, to free it from excess of iodine, and dried, presents the appearance of a black shining mass exhibiting a coppery lustre. Perfectly dry iodide of starch may be heated for several days to a temperature of 100° without undergoing decomposition; it may, therefore, be regarded as a very stable body. In the presence of moisture, however, it is decomposed, with, if heated in closed vessels, formation of hydriodic acid, whilst, if it be heated in open vessels, part of the iodine is volatilised, the remainder being converted into hydriodic acid.

Iodide of starch is also formed when dry starch and an alcoholic solution of iodine are triturated in a mortar, provided the alcohol contains water; with absolute alcohol a brown colour is produced, which, on addition of water, changes to blue. Iodide of starch is not formed when iodine vapour is passed over dry starch, but by using moist starch the iodide is formed; from this it would appear that water is necessary to the formation of iodide of starch (Stocks, Chem. News, 56, 212; 57, 183).

It is also formed from a mixture of potassium iodide and starch paste by the action of such reagents as liberate iodine from its compounds. Such are chlorine, bromine, nitric acid, strong sulphuric acid, ferric chloride, potassium permanganate, &c., all of which cause the characteristic blue colour to appear. The blue colour of iodide of starch is destroyed in presence of excess of chlorine or bromine, owing to the formation of iodine chloride or bromide.

Starch granules have a greater attraction for iodine than unorganised starch. Hence a cold clear solution prepared from crushed starch granules, and coloured blue by iodine, is completely decolorised by adding whole starch granules; similarly starch granules attract iodine more energetically than dextrin (Bruckner, Monatsh. 4, 889–912).

Iodide of starch is soluble only in a large quantity of water, but as ordinarily prepared from starch paste it is an opaque mass, and when examined under the microscope presents the appearance of blue flocculent masses of the iodide floating about in the liquid portion. In this state the blue colour is destroyed by heat (Stocks, Chem. News, 56, 212; Tomlinson, Phil. Mag. [v.] 50, 168), but the change is gradual, the liquid becoming first greenish, then yellowish, and finally colourless, and if at this point it be allowed to cool the blue colour does not again appear, although it does so if the heating be discontinued at the yellowish stage and the liquid be allowed to cool; this decolorisation is due to the formation of hydriodic acid.

When iodide of starch does not contain an excess of iodine, alcohol, ether, carbon disulphide, or benzene fail to extract any iodine from it; if, however, the iodide be heated with alcohol it becomes rapidly decolorised, ethyl iodide being formed at the same time.

The colour produced by iodine and starch grains has been found to vary slightly with the nature of the starch, potato starch giving a deep blue, whilst wheat starch gives a colour inclining somewhat to violet.

The exact composition of starch iodide has not been definitely settled. According to F. Mylius, iodide of starch contains 19·69 p.c. of iodine, and has the formula $(C_{24}H_{40}O_{20}I)_4HI$; whilst F. Seyferth finds 18·56 p.c. of iodine, formula $(C_{24}H_{40}O_{20})_6I_7$; and G. Rouvier fixes the iodine content at 19·6 p.c., and formula $(C_6H_{10}O_5)_{16}I_5$.

Syniewski deduces the formula of the iodide from his experiments, making use of his formaldehyde amylodextrin

$$[(C_{54}H_{90}O_{45}+1\tfrac{1}{2}H_2O)I_3]_4,$$

which corresponds with 20·5 p.c. of iodine. He suggests that the iodine probably attaches itself to the terminal CH_2OH groups (see The Constitution of Starch, v. Syniewski, Annalen, 1902, 324, 212–268).

Harrison (Chem. Soc. Proc. 1910, 26,

252–253) has put forward a new theory to explain the starch-iodine reaction. He finds that the presence of iodides is not necessary for the formation of starch iodide, but the depth of colour is increased by the presence of any salt or weak acid. The gradual addition of alcohol changes the blue to violet, red, orange, and yellow, the reverse change taking place on dilution with water. The same colour change is produced by carefully heating the blue solution, the reverse phenomena being observed on cooling.

He shows that all the iodine can be removed from starch iodide by washing with pure water, and draws the conclusion that the blue solution of iodine and starch is a colloidal solution of iodine, the starch acting as a protective colloid.

13. *Action of other reagents.* Potassium permanganate exercises a powerful reducing action on starch, but instead of dextrin a series of gummy acids are produced, which reduce Fehling's solution only to a very slight extent. Powdered potassium permanganate is added to a 2½ p.c. starch paste; much carbonic acid is evolved, and manganese dioxide precipitated. The solution is filtered, neutralised with acetic acid, concentrated lead acetate solution added, the resulting precipitate washed with hot water, decomposed with hydrogen sulphide, the solution concentrated and poured into absolute alcohol, when a curdy precipitate is formed. This is washed with absolute alcohol and ether, and dried *in vacuô* over sulphuric acid. The bodies formed possess dextrorotatory powers, which vary according to the quantity of permanganate employed, and give reactions with iodine from reddish-violet, through reddish-brown, to brown. The elementary analysis of a product which was not coloured by iodine agreed with the formula $C_{12}H_{22}O_{11},C_{12}H_{20}O_{10}$ (Lintner, Zeitsch. angew. Chem. 1890, 546).

Formaldehyde cause the starch grains to gradually swell to a thick jelly, which ceases to give a colouration with iodine, becoming limpid after several days, and capable of filtration after a few months. This filtrate, when allowed to evaporate spontaneously, solidifies to a crystalline mass, which is a compound of starch and formaldehyde and polymerised formaldehyde. When warmed both free and combined formaldehyde volatilise, leaving a substance which gives a blue colour with iodine, and which, on analysis, gives values agreeing with the formula

$$[C_{54}H_{90}O_{45}+1\tfrac{1}{2}H_2O]_4,$$

and which Syniewski considers to be identical with his amylodextrin. The action of formaldehyde in a concentrated solution of starch is considered to be a carbinol hydrolysis, the product 'formaldehyde amylodextrin' being hydrolised with extreme ease (*v.* Syniewski, Annalen, 1902, 324, 201).

When chloroform is added to a solution of starch in zinc chloride and allowed to remain three months the whole of the starch is converted into dextrin.

When starch paste is treated with chloroform a soluble modification of starch similar to that obtained by the action of hydrochloric acid is formed, and on heating a mixture after some months the starch dissolves and separates as a fine paste on cooling.

On shaking 1 part of starch with 100 parts of a solution of chloral hydrate (10 parts water to 7 parts chloral hydrate) an almost clear viscous solution is obtained, which does not give a blue colouration with solid iodine or a solution of iodine in chloral hydrate.

Tannic acid gives a flocculent leathery precipitate with starch paste, as well as with soluble starch, which is soluble in boiling water but is reprecipitated on cooling.

14. *Action of enzymes.* Certain enzymes exert a most powerful action on gelatinised starch, as well as on some of the varieties of starch in the raw state. Of these, the most active are the diastase of malted barley, the saliva, and the pancreatic juice.

If the action of a solution of any one of these ferments on starch paste be watched, the first effect produced will be complete liquefaction of the paste, and the production, in an incredibly short space of time, of a perfectly limpid liquid. At this instant, if the liquid be tested with iodine, a reaction for pure soluble starch may be observed; immediately following this comes the saccharification of the soluble starch. The blue colour produced by iodine disappears, giving place to a reddish-brown colour, indicating the presence of erythrodextrin, which in turn becomes transformed into achroodextrin, when iodine ceases to impart any longer a colour to the liquid. At the same time, concurrently with the disappearing of the starch, the proportion of sugar goes on increasing, and continues to do so for a considerable time after the iodine has ceased to show any reaction.

Although starch in some form or other enters so largely into the food of man and beast, it was not until early in the last century that it received any attention from the hands of chemists. Since that time, however, much attention has been bestowed upon the changes which it undergoes under the influence of heat, acids, and certain vegetable and animal extracts, and much valuable information has resulted therefrom.

Considering the very important part which starch plays in several industrial processes on the one hand, and how a careful study of its various transformations serves to throw very considerable light upon many questions connected with vegetable, as well as animal, physiology, it will, perhaps, not be altogether out of place to give, as briefly as possible, a history of the transformations of starch from the earliest up to the present time.

15. *History of starch transformations.* In the year 1811 Vauquelin discovered that when starch is heated to a high temperature it is converted into a substance completely soluble in water, and which resembles gum arabic in many of its physical properties. In the following year Vogel found that a similar substance is formed when starch is acted upon by hot dilute acid. About the same time, Kirchoff discovered that starch, when boiled with dilute sulphuric acid, yields a crystallisable sugar; and two years later, in 1814, the same chemist observed that a similar transformation is brought about by the action of the vegetable albumin of grain, and also that the action of this substance is much intensified by subjecting the grain to the malting process.

The gummy substance produced from starch by the action of dilute acid was first carefully examined in 1833 by Biot and Persoz, who gave to it the name of *dextrin*, from the property which it possesses of rotating a polarised ray of light strongly to the right.

Biot and Persoz did not look upon dextrin as a decomposition product of starch, but considered it rather as consisting of the contents of the starch granules freed from their outer coating by the action of the acid. Payen and Persoz—sharing the same view as to the formation of dextrin from starch by the action of an infusion of malted grain, and which they attributed to the presence of a particular transforming agent—named it *diastase*, from its supposed property of separating the interior of the starch granules from their outer envelope. They were the first chemists who prepared dextrin from starch by the action of diastase, and describe it as a substance soluble in cold water and in weak alcohol, and as not coloured by iodine. A few years later Payen stated that the specific rotatory power of his dextrin was equal to that of starch, and that its elementary composition was indicated by the formula $C_6H_{10}O_5$.

He also came to the conclusion that the dextrins produced by the action of dilute sulphuric acid, diastase, and heat respectively were simply physical modifications of one and the same substance.

Up to the year 1860, dextrin was considered as occupying an intermediate position between starch and sugar, the starch being first converted into dextrin, and this, by subsequent hydration, into sugar. But at this period, Musculus brought forward evidence to prove most conclusively that dextrin and sugar are not successively formed products, but are produced simultaneously by a splitting up of the starch molecule. This theory, which met with strong opposition at first, is now generally admitted to be in the main correct.

The dextrin described more in detail by Musculus in 1865 was a body not coloured by iodine, and did not reduce Fehling's solution. It now began to be recognised amongst chemists that there are at least two dextrins derivable from starch—the one coloured red by iodine, and the other giving no colouration with that reagent. These were described by Griessmayer in 1871 as dextrin I. and dextrin II., and in the following year O'Sullivan distinguished them as α and β dextrin. These are now more generally referred to as erythrodextrin and achroodextrin respectively, names first proposed by Brücke in 1872 as indicative of their behaviour with iodine.

In a series of most interesting and important researches extending from 1872 to 1876 (Chem. Soc. Trans. 25, 579; 29, 479; 30, 125), O'Sullivan proved most satisfactorily that the sugar produced by the action of diastase or acid on starch is not, as had up to this time been generally supposed, dextrose, but is a sugar of the saccharose type, having a considerably higher specific rotatory power than dextrose, and a much less reducing action upon Fehling's solution.

This body had been previously isolated, as far back as the year 1819, by De Saussure, who, however, merely described its crystalline appearance. It was prepared in 1847 by Dubrunfaut, who, from its optical properties, recognised it as a distinct sugar and named it *maltose*. His observations, however, obtained but little notice at the time of their publication, and appear to have been entirely forgotten until the re-discovery of maltose by O'Sullivan in 1872 (Chem. Soc. Trans. 25, 579). This investigator also gave the results of his examination of the dextrins prepared by the action of diastase and of acid upon starch. These results led him to the conclusion that the dextrins from both sources possess the same specific rotatory power of $[\alpha]_j = +213°$, and have an elementary composition corresponding to the formula $C_6H_{10}O_5$, and although he did not succeed in obtaining any of the dextrins absolutely free from a reducing action on Fehling's solution, yet he adduced good evidence to show that in a state of purity they would possess no reducing action. Both of these dextrins are slowly converted into maltose by the action of diastase.

In 1875 Bondonneau, apparently unaware of the previous work of O'Sullivan, described three dextrins, which he denotes as α, β, and γ dextrins respectively. The first of these corresponds to O'Sullivan's α dextrin and Brücke's erythrodextrin, whilst β dextrin appears to be an achroodextrin. Both of them possess a much lower specific rotatory power than O'Sullivan's, doubtless owing to not being as completely purified. There can now be no doubt that his γ dextrin was nothing more or less than maltose, and as Bondonneau regarded the reducing sugar formed throughout to be dextrose, it is easy to understand that he should fall into such an error with regard to his γ dextrin.

The properties of dextrin and maltose having been thus definitely established, and it having been shown conclusively that these two substances were the only products obtained by the action of diastase upon starch paste under ordinary conditions, the attention of investigators was turned to the influence of time and temperature upon the reaction by which these substances are produced, so that in the history of starch transformation a new field of research was opened up in 1876 by O'Sullivan (Chem. Soc. Trans. 30, 125). According to this investigator, starch granules which are intact are unacted upon by diastase or the cold water extract of malt; gelatinised starch, however, either in the cold or at temperatures up to 72° is readily transformed. He also established the fact that the transformation of starch into dextrin and maltose is not a gradual act of hydration, the dextrin appearing first and the maltose afterwards, but that the two bodies are formed simultaneously, and in certain proportions according to the conditions under which the starch molecule splits up. On this assumption, the splitting up of the starch molecule by diastase takes place according to certain definite equations, the relative proportion of the decomposition products depending upon the temperature at which the transformation takes place, so that, starting with soluble starch, it is possible to obtain a series of equations, each succeeding one containing a molecule less of dextrin and a molecule more of maltose than the one immediately preceding it until we arrive at the final equation. According to O'Sullivan, the following reactions take place:—(*a*) When starch is acted on by malt extract at any temperature below 63°, if the solution be immediately (5–10 minutes) cooled and filtered, the product invariably contains maltose and dextrin in proportions closely agreeing with 67·85 p.c. of the former and 32·15 p.c. of the latter; $K=44\cdot1$, $[\alpha]_j=170\cdot6°$, and this reaction is represented by O'Sullivan's equation A.

$$\underset{\text{Starch}}{(C_{12}H_{20}O_{10})_6}+4H_2O=\underset{\text{Maltose}}{(C_{12}H_{22}O_{11})_4}+\underset{\text{Dextrin}}{(C_{12}H_{20}O_{10})_2}$$

(*b*) When starch is acted on by malt extract at any temperature between 64° and 68°–70°, if the solution be immediately cooled and filtered the product invariably contains maltose and dextrin in proportions agreeing closely with 34·54 p.c. of the former and 65·46 p.c. of the latter; $K=22\cdot4$, $[\alpha]_j=191\cdot8°$, and corresponding to the equation B.

$$\underset{\text{Starch}}{(C_{12}H_{20}O_{10})_6}+2H_2O=\underset{\text{Maltose}}{(C_{12}H_{22}O_{11})_2}+\underset{\beta\text{ Dextrin}}{(C_{12}H_{20}O_{10})_4}$$

(*c*) When starch is acted on by malt extract at temperatures from 68°–70°C. to the point at which the activity of the transforming agent is destroyed, if the solution be cooled and filtered at the end of 5–10 minutes, the product contains maltose and dextrin in proportions agreeing closely with 17·4 p.c. of the former and 82·6 p.c. of the latter; $K=11\cdot3$, $[\alpha]_j=202\cdot8°$, and corresponding to equation C.

$$\underset{\text{Starch}}{(C_{12}H_{20}O_{10})_6}+H_2O=\underset{\text{Maltose}}{C_{12}H_{22}O_{11}}+\underset{\alpha\text{ Dextrin}}{(C_{12}H_{20}O_{10})_5}.$$

O'Sullivan considers that the formula for soluble starch must be at least six times the $C_{12}H_{20}O_{10}$ molecule, and that it, as well as the dextrins which are produced from it by the action of diastase, are a series of bodies of the same molecular weight in which the difference in their behaviour to this agent must be accounted for by a difference of relation in the arrangement of the molecules to one another, probably in solution alone.

In 1879 Brown and Heron (Chem. Soc. Trans. 35, 596), whilst confirming to a large extent O'Sullivan's results, came to the conclusion that the transformations of starch are to be represented by at least ten equations, of which they considered that their experiments substantiated at least four well-defined molecular transformations, by far the best-defined and most stable being the reaction obtained when starch paste is heated with malt extract at 60° for 30 minutes,

$$K_{3\cdot86}=49\cdot3,\ [\alpha]_{j3\cdot86}=162\cdot5°.$$

The next fixed point is that of the disappearance of the iodine reaction for erythrodextrin when starch paste is transformed with malt extract heated to 66°. This takes place when $K_{3\cdot86}=25\cdot0$ and $[\alpha]_{j3\cdot86}=188\cdot5°$ or thereabouts, and is very constant with varying quantities of malt extract.

The next strongly-marked reaction is that obtained with malt extract heated to 75°, the numbers obtained being $K_{3\cdot86}=18\cdot9$, $[\alpha]_{j3\cdot86}=195°–196°$.

The highest stable transformation is obtained by the action of malt extract heated to 66° and made very slightly alkaline with sodium hydroxide, the same reaction being also marked in all transformations above 66° by the appearance of the maximum iodine colouration for erythrodextrin, the numbers for this transformation $K_{3\cdot86}=12\cdot7$ and $[\alpha]_{j3\cdot86}=202°–203°$ are very nearly those of O'Sullivan's equation C.

It was also found that when higher conversions are treated with unheated malt extract at 50°–60° they are very rapidly converted into the lower form $K_{3\cdot86}=49\cdot3°$, $[\alpha]_{j3\cdot86}=162\cdot5$, at which points these factors remain for a time constant.

Brown and Heron conclude that the dextrins are not metameric but polymeric bodies; those corresponding to transformations of high optical activity being of greater molecular complexity than those yielded by transformations of lower optical activity, the latter being produced from the former by a partial act of hydration with consequent elimination of maltose. About the same time Musculus and Gruber (Bull. Soc. chim. [ii.] 30, 69) brought forward a similar theory. They look upon starch as a polysaccharide, having for its formula $n(C_{12}H_{20}O_{10})$, and undergoing under the influence of diastase successive hydrations and decompositions.

As the result of their experiments Brown and Heron were led to adopt the formula $10(C_{12}H_{20}O_{10})$ for soluble starch.

The first action of the transforming agent upon this complex and unstable molecule results in the removal by hydration of one of the groups of $C_{12}H_{20}O_{10}$, thus producing maltose, whilst the remaining nine groups, $C_{12}H_{20}O_{10}$, constitute the first dextrin of the series, erythrodextrin *α*. This dextrin, in its turn, on further hydration splits up into a molecule of maltose and erythrodextrin *β*, consisting of eight $C_{12}H_{20}O_{10}$ groups, and so in this way the degradation of the original molecule proceeds, until by successive stages of hydration the lowest equation is reached. The following table represents these transformations:—

TABLE VIII.

No. of Transformation	Maltose	Dextrin	$[\alpha]_{j3\cdot86}$	$K_{3\cdot86}$
Soluble starch .	0	0	216·0	0
Equation 1 .	10·4	89·6	209·0	6·4
,, 2 .	20·8	79·2	202·2	12·7
,, 3 .	31·0	69·0	195·4	18·9
,, 4 .	41·3	58·7	188·7	25·2
,, 5 .	51·3	48·7	182·1	31·3
,, 6 .	61·1	38·9	175·6	37·3
,, 7 .	71·0	29·0	169·0	43·3
,, 8 .	80·8	19·2	162·6	49·3
,, 9 .	90·3	9·7	156·3	55·1
Maltose . .	100·0	0·0	150·0	61·0

In 1879 Herzfeld (Ber. 1879, 2120) found that in addition to maltose and dextrin a third substance, maltodextrin, was under certain circumstances formed by the action of diastase upon starch paste. This compound was regarded by him as being intermediate between achroodextrin and maltose; it was insoluble in alcohol of 90 p.c., and completely fermentable by yeast, possessing a specific rotatory power $[\alpha]_j=171\cdot6$, $K=23\cdot5$. It was further investigated by Brown and Morris (Chem. Soc. Trans. 47, 527). They found that when the action of malt extract on starch paste is limited there is always found amongst the products of transformation, besides maltose and dextrin, a third substance which is more soluble in alcohol than the dextrins, and has a specific rotatory power of $[\alpha]_{j3\cdot86}=193\cdot1$ and a cupric reducing power of $K_{3\cdot86}=21\cdot1$, corresponding to an apparent composition of 34·6 p.c. maltose and 65·4 p.c. dextrin. It is completely hydrated to maltose by the action of malt extract at 50°–60°.

Maltodextrin is not fermentable by yeast (*S. Cerevisiæ* of the high fermentation), but is slowly hydrolysed into maltose and thus rendered fermentable by certain forms of saccharomyces of the secondary fermentation (*S. Pastorianus*, *S. ellipticus*). Brown and Morris considered that maltodextrin was not, as supposed by Herzfeld, a mere hydration product of achroodextrin, but was produced from starch and the polymeric dextrins by the fixation of a molecule of water upon the ternary group $(C_{12}H_{20}O_{10})_3$, of which there could not be less than five in the starch molecule, which resulted in the separation from the dextrin residue of maltodextrin

$$C_{12}H_{22}O_{11}.$$

This by the fixation of two more molecules of water gave rise to freely fermentable and crystallisable maltose.

Further experiments in connection with this subject have induced Brown and Morris to alter their views with regard to the dextrins (Chem. Soc. Trans. 53, 610; 55, 450, 462; Trans. Lab. Club. 3, 81), which they consider are, after all, not polymeric but metameric, and from their investigations they have built up the following hypothesis, which appears to them to be more in accord with the facts than any other yet propounded.

The starch molecule may be pictured as consisting of four complex amylin groups arranged round a fifth similar group constituting a molecular nucleus.

The first action of diastase is to break up this complex group and liberate all the five amylin groups. The central amylin nucleus, consequent on a closing up of the molecule, withstands the further influence of hydrolysing agents, and constitutes the stable dextrin of No. 8 equation. The four outer amylin groups are capable, when liberated, of being rapidly and completely converted into maltose by successive hydrolyses through a series of amyloïns or maltodextrins, the number of which is only limited by the size of the original amylin group.

In 1891 C. J. Lintner (Zeit. ges. Brau. 1891, 284) discovered a sugar amongst the products of starch hydrolysis, which yielded an osazone readily soluble in hot water, and melting at 152°–153°, which he called iso*maltose*.

Subsequently Lintner and Düll found that after the maltose had been removed from the products of starch conversion by fermentation, they were able by repeated precipitation with alcohol to resolve the unfermented matters into dextrin and *iso*maltose, no trace of an intermediary dextrin being found. They describe iso*maltose* as an intensely sweet tasting body having an optical rotatory power in a 10 p.c. solution $[\alpha]_D+139°–140°$ and $K=50\cdot63$. Their hypothesis of starch, transformed with diastase, starting from soluble starch, is as follows:—

I. $(C_{12}H_{20}O_{10})_{54}+3H_2O$
$=3[(C_{12}H_{20}O_{10})_{17}\cdot C_{12}H_{22}O_{11}]$.

II. $3[(C_{12}H_{20}O_{10})_{17}\cdot C_{12}H_{22}O_{11}]+6H_2O$
$=9[(C_{12}H_{20}O_{10})_5\cdot C_{12}H_{22}O_{11}]$.

III. $9[(C_{12}H_{20}O_{10})_5\cdot C_{12}H_{22}O_{11}]+45H_2O$
$=54C_{12}H_{22}O_{11}$ = Isomaltose.

IV. $54C_{12}H_{22}O_{11}$ = Maltose.

They considered that this action proceeded irregularly, some of the soluble starch molecules being broken down much more rapidly than others, the presence of maltose and the higher dextrins in high-angled transformations being explained by this means.

In 1892 Schifferer, working on the same lines as Lintner, practically confirmed his views with regard to *iso*maltose.

In 1893 Lintner and Düll described the properties of several bodies which they had isolated from the products of starch transformation after long and tedious fractionation with alcohol of different strengths. These were as follows:—

Amylodextrin. A loose white powder slightly soluble in cold water, readily soluble in hot water. $[\alpha]_D=+196$, does not reduce Fehling's solution, and gives a deep colouration with iodine, and is the principal constituent of soluble starch. The formula is given as $(C_{12}H_{20}O_{10})_{54}$.

Erythrodextrin. This body is readily soluble in water $[\alpha]_D=+196$, reducing power, R 1=1 p.c. that of maltose, and gives a reddish-brown colour with iodine. The formula given is

$$(C_{12}H_{20}O_{10})_{17}\cdot C_{12}H_{22}O_{11},$$

and it is formed from amylodextrin as follows:

$$(C_{12}H_{20}O_{10})_{54}+3H_2O=3[(C_{12}H_{20}O_{10})_{17}\cdot C_{12}H_{22}O_{11}]$$

Achroodextrin I. This dextrin is soluble in water; $[\alpha]_D+192$, reducing power R.10=10 p.c. that of maltose, and gives no colouration with iodine. The formula given is:

$$(C_{12}H_{20}O_{10})_5\cdot C_{12}H_{22}O_{11},$$

and it is formed from erythrodextrin as follows:

$$3[(C_{12}H_{20}O_{10})_{17}\cdot C_{12}H_{22}O_{11}]+6H_2O$$
$$=9[(C_{12}H_{20}O_{10})_5C_{12}H_{22}O_{11}].$$

Achroodextrin II. Only found in very small quantities in transformation products by the action of diastase $[\alpha]_D=+180$, reducing power R 24=24 p.c. that of maltose.

In 1895 Ost (Chem. Zeit. 1895, 1501) investigated the dextrins in a starch transformation, and isolated a dextrin having a rotatory power $[\alpha]_D=+180°–183°$, and reducing power R 28–33, and gave as its formula $C_{36}H_{62}O_{31}$. This he believed to be identical with Lintner and Düll's achroodextrin II., and to be contained in Brown and Morris' maltodextrin $[\alpha]_{D3\cdot86}+171°$ (R=34). He made the observation that it was improbable that dextrins of absolute purity could be prepared, as it is extremely probable that they may undergo some little change during the process of isolation.

In 1895 Ling and Baker (Chem. Soc. Trans. 1895, 43, 702) published the results of their investigations on the *iso*maltose discovered by Lintner, which threw much doubt on the existence of this product.

Working with diastase prepared from air-dried malt on the same lines as Lintner and Düll they obtained a substance having a sweet but by no means intensely sweet taste, with an optical rotatory power of $[\alpha]_{D3\cdot86}+144\cdot5°$, and $K=48\cdot59$. It yielded an osazone having a m.p. between 160° and 170°, and the results of its ultimate analysis and its molecular weight gave figures which indicated a disaccharide. When submitted to the action of diastase it showed an optical rotatory power of $[\alpha]_{D3\cdot86}$ $+131\cdot2°$, and $K=57\cdot64$, these changes not being accompanied by any change in the specific gravity of the solution. They concluded that Lintner's '*iso*maltose' was a mixture of maltose and a simple dextrin, having the formula

$$C_{12}H_{22}O_{10}+H_2O.$$

When working with diastase obtained from high-dried malt they obtained a substance yielding an osazone having a melting-point identical with Lintner's *iso*maltosazone, which analysis showed to be an osazone of a trisaccharide. They also found a certain amount of glucose was produced in transformations with diastase obtained from kiln-dried malts.

In a later paper, Ling and Baker (Chem. Soc. Trans. 1895, 43, 739) showed that the osazone obtained from the so-called *iso*maltose could be fractionated by recrystallisation into portions having melting-points corresponding to maltosazone and a substance which analysis indicated to be a disaccharide, and which they regarded as impure maltosazone. The presence of glucose was always detected in starch transformations with diastase from kiln-dried malt, but the osazones from the transformation products soluble in 90 p.c. alcohol were characteristic of Lintner's *iso*maltose, and gave analytical results between those required for the osazone of a disaccharide and that of a trisaccharide. It thus appeared as if a trisaccharide was a product of the action of diastase from kiln-dried malt. As an explanation of this they suggest that the trisaccharide might be formed by the condensation of a molecule of a simple dextrin with one of glucose under the influence of phenylhydrazine.

Brown and Morris, also in 1895 (Chem. Soc. Trans. 1895, 43, 702), published results of their investigations which threw doubt on the existence of *iso*maltose, first pointing out that it does not conform to their 'law of definite relation.' This law was the outcome of H. T. Brown's work in conjunction with others up to this date, and was as follows: The composition of the mixed products of a starch transformation by diastase or of any fractionated portions of such products can always be consistently interpreted in terms of maltose, having an opticity of $[\alpha]_{j3\cdot86}+150°$, and a reducing power of $K_{3\cdot86}$ 61, and a non-reducing dextrin having an opticity of $[\alpha]_{j3\cdot86}+216°$.

Lintner's *iso*maltose has an optical activity equivalent to $[\alpha]_j+156°$ and K 48·8. According to the law this optical rotatory power requires a reducing power of K 55·3; and a reducing power of K 48·8 requires an optical rotatory power of $[\alpha]_j+163\cdot2$. They came to the conclusion that *iso*maltose could be split up by fractionation, fermentation, &c., in such a manner as to indicate that it was a mixture of maltose and bodies of the amyloin type.

A study of the osazone led them to the belief that it was maltosazone modified in its crystalline structure and melting-point by the presence of an impurity, and they were able to compel maltosazone to crystallise in the *iso*maltose form by the addition of a trace of an amorphous product of the reaction. They found that 50–60 p.c. of *iso*maltose was fermentable, and their investigations led them to believe that the matter fermented was maltose, and the unfermented portion approaches very closely in composition that of an amyloïn containing two amylon groups and one amylin group.

In the same year Ost (Chem. Zeit. 1895, 1501), following the instructions of Lintner and Düll, made an attempt to isolate *iso*maltose. He found that their methods were not satisfactory, and after removing the maltose from the alcoholic extracts by means of crystallisation, he obtained osazones from the residue similar to those said to be characteristic of *iso*maltose, but which on further investigation proved to be maltosazone. He confirmed Ling and Baker's views, that mixtures of maltose and dextrin, when heated together, produced an osazone simulating *iso*maltosazone. No osazone was obtained in starch transformations where the whole of the maltose had been removed by fermentation, and from those in which a portion of the maltose had been left unfermented he obtained osazones similar to *iso*maltosazone. Ost's conclusions agreed with those of Ling and Baker, and Brown and Morris in that *iso*maltose has no real existence, and that the *iso*maltosazone of Lintner and Düll is modified maltosazone.

He came to the conclusion, after an investigation into the products of starch transformation by diastase, that starch itself has the composition $(C_{12}H_{20}O_{10})_n$, n indicating a large but unknown number. He freely criticises the results and theories put forward by previous workers, holding the non-reducing dextrin of Brown and Morris to be non-existent, and that their law of 'definite proportion' is not always fulfilled even in their own experiments, and is certainly not in the achroodextrin II. which he had prepared. He considers that the theory of Brown and Heron should have been entirely abandoned instead of being altered to the amyloin theory after maltodextrin and amylodextrin had been recognised as individual substances. He threw doubt on the molecular weight determinations, especially those of the higher dextrins, and regarded erythrodextrin as a mixture of starch and achroödextrin.

Mittelmeier (Zeitsch. angew. Chem. 1895, 552) put forward a theory based on his investigations that the starch molecule under the action of diastase is split up into two amylodextrins, which he terms primary and secondary erythrodextrin. The primary erythrodextrin is rapidly converted into maltose in the time that the secondary reached the stage in which it gives a red colouration with iodine, in this way he explains the presence of the highest dextrins and maltose in the same starch conversions. The optical rotatory power of these erythrodextrins is about $[\alpha]_D+170°$; they both reduce Fehling's solution and form osazones. Under the influence of diastase primary and secondary achroodextrins are obtained.

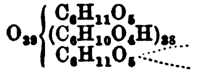
In 1897 Ling and Baker (Chem. Soc. Trans. 1897, 71, 509) gave some further results of an examination of the products of the limited action of diastase on potato starch paste at 70°. They obtained the following dextrins:

Maltodextrin-α $C_{24}H_{22}O_{11}$ (identical with that of Brown and Morris) having optical and reducing powers of $[\alpha]_D+180°$; R 32·81.

Maltodextrin-β $C_{24}H_{42}O_{21}$ (identical with a body isolated by Prior in 1896 (Bayer, Brauer, 1896, 157), which he termed achroodextrin III.) having the constants $[\alpha]_D+171{\cdot}6°$; R 43.

From the fraction designated *iso*maltose by Lintner an unfermentable substance was obtained, having the constants $[\alpha]_D+156°$; R 62·5, which probably consists principally of a substance having the formula $C_{12}H_{22}O_{11}$.

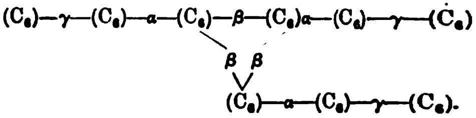
In 1898–1899 Brown and Millar (Chem. Soc. Trans. 1899, 75, 286–337) tried to isolate the intermediate products of saccharification by conversion into nitric acid esters. Owing to oxidation, however, this was unsuccessful; but by moderate oxidising agents dextrinic acids were obtained. Starting with the maltodextrin of Brown and Morris they first obtained an acid which they termed 'maltodextrinic acid A.' This can be hydrolised in two successive steps, by diastase and acids respectively, into first an acid which they term maltodextrinic acid-β, together with maltose, and, secondly, into a pentose acid and glucose. In further experiments they obtained a dextrin with optical and reducing properties corresponding to $[\alpha]_D 195°–195{\cdot}7°$; R 5·7–5·9, which they claim is a stable dextrin, proving this statement by the products of oxidation. On the data furnished by their researches they base their theory that the dextrin molecule may be empirically regarded as made up of 39 $C_6H_{10}O_5$ groups in combination with a terminal $C_6H_{12}O_6$ group; or in other words, a condensation of fatty glucose molecules with the elimination of $39H_2O$, the constitutional formula being—



$$O_{39}\left\{\begin{array}{l}C_6H_{11}O_5\\(C_6H_{10}O_4H)_{38}\\C_6H_{11}O_5\end{array}\right.$$

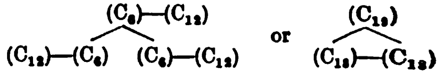
In 1900 and 1902 V. Syniewski (Annalen, 1900, 309, 282; 1902, 324, 212) brought forward a new theory on the breaking down of the starch molecule by hydrolysis. He points out that starch can be hydrolised in two ways, either so as to yield substances which do not reduce alkaline copper solutions (carbinol hydrolysis), or those which do reduce alkaline copper solutions (carbonyl hydrolysis). The simplest product of the carbinol hydrolysis of starch is a substance amylogen $C_{54}H_{90}O_{45}$, which is obtained by the action of sodium peroxide on potato starch. He finds that by heating starch paste at 140° in an autoclave carbinol hydrolysis occurs and proceeds as far as amylodextrin $C_{216}H_{372}O_{186}$. By treating this amylodextrin with malt extract previously heated at 78° for 18 minutes the solution contained exclusively a product identical with the maltodextrin of Brown and Morris, the achroodextrin II. of Lintner and Düll, and the maltodextrin-α of Ling and Baker, and which he denotes limit dextrin II. Elementary analysis and determination of the molecular weight established the formula $C_{36}H_{62}O_{31}$, having constants $[\alpha]_D 179{\cdot}36°$; R 30. Further hydrolysis of this product with malt extract to a point where the reducing power of the dissolved bodies was R 60 gave a product consisting mainly of a compound $C_{24}H_{42}O_{21}$, which was identical with Prior's achroodextrin III., and Ling and Baker's maltodextrin-β, which he called γ-maltodextrin, having constants $[\alpha]_D 172{\cdot}17°$; R 42·7. Both limit dextrin II. and γ-maltodextrin on complete hydrolysis with malt extract yield a mixture of maltose and *iso*maltose or, as the author terms it, dextrinose $C_{12}H_{22}O_{11}$, with constants $[\alpha]_D 141{\cdot}4°$; R 84·5.

Syniewski considers the theories of Lintner and Düll and of Brown and Morris on the mechanism of starch hydrolysis to be untenable, and elaborates a theory of his own. He regards the starch molecule as made up of amylogen residues, and he assumes that the nine glucose groups which make up the amylogen residue $C_{54}H_{90}O_{45}$ in the starch molecule are connected together by nine carbonyl bonds of three different kinds which he denotes as α-, β-, and γ-bonds. The amylogen residue may be thus represented—



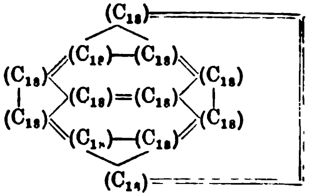
$$\begin{array}{l}(C_6)-\gamma-(C_6)-\alpha-(C_6)-\beta-(C_6)\alpha-(C_6)-\gamma-(\dot{C}_6)\\ \qquad\qquad\qquad\qquad\qquad\beta\ \ \beta\\ \qquad\qquad\qquad\qquad\qquad(C_6)-\alpha-(C_6)-\gamma-(C_6).\end{array}$$

The three monocarbonyl bonds which unite three maltose residues with the residue of limit dextrin I. are α- bonds. The three monocarbonyl bonds which are between the three glucose groups of the limit dextrin I. residue are β-bonds, and those bonds which unite the glucose groups of the maltose residues are γ- bonds. The amylogen residue may also be represented as follows:—



$$\begin{array}{ccc}\begin{array}{c}(C_6)-(C_{12})\\(C_{12})-(C_6)\quad(C_6)-(C_{12})\end{array} & \text{or} & \begin{array}{c}(C_{18})\\(C_{18})-(C_{18})\end{array}\end{array}$$

The composition of starch is represented by the formula $[(C_{54}H_{96}O_{48})_n—3H_2O)$, whilst that of amylodextrin is represented by the formula $n[C_{54}H_{90}O_{45}+1\frac{1}{2}H_2O)$. By the action of malt extract heated to 78° amylodextrin may be completely converted into limit dextrin II. $C_{36}H_{62}O_{31}$. From this it follows that n must be a whole number. Limit dextrin II. is formed from two different amylogen residues, and this conclusion is arrived at from the assumption that the β- carbonyl bonds are disrupted in its formation. From certain geometrical considerations the value of n in the potato starch molecule is considered to be 4, its empirical formula being $C_{216}H_{368}O_{180}$, which is thus graphically represented—



According to this formula each amylogen residue in the starch molecule is united by six carbinol anhydride bonds, three of these being between limit dextrin I. residue and three between maltose residues. The former are denoted *d*- bonds, the latter *m*- bonds. The single lines between the C_{18}- groups forming a dextrin ring are *β*- carbinol bonds; the double lines uniting two C_{18}- groups are carbinol bonds, one being a *d*- bond and the other an *m*- bond. It is conceivable that the molecular constitutions of other starches are analogous but contain a different number of amylogen residues, thus 2, 8, or 20. The author goes on to explain the several steps in the process of hydrolysis of the starch molecule, for which the reader is referred to the original papers or extracts of same in Jour. Inst. Brew. 1900, 6, 110; and 1902, 8, 732–737.

There is no doubt that much of the obscurity and confusion which has arisen in the interpretation of results up to this period has its origin in the fact that starch has been too generally regarded as a chemically uniform substance. From about this time onward most of the work on starch has been directed to the investigation of the nature and structure of the starch granule, and also to a closer study of the transforming enzyme *diastase*.

Pottevin (Annales de l'Instit. Pasteur, 1899, 665, 728, and 796) was among the first to work on these lines. He found two distinct phases in the saccharification of starch paste, one of extraordinary rapidity, and the other increasingly sluggish, and from among the possible causes of retardation he dismisses the weakening of the enzyme and the inhibitive effect of the soluble products, forming the conclusion that since the slackening refers to the production of dextrins as well as maltose, the lack of uniformity must exist in the starch itself.

In 1902 Ling and Davis (J. Inst. Brewing, 1902, 8, 475) showed that the unrestrained action of diastase at the temperature at which its activity is at its optimum, namely 55°, carried the transformation of starch paste to a point at which the constants of the substances in solution were substantially those of maltose. They formed the opinion that the so-called No. 8 equation of Brown and Heron is not really a resting stage in the reaction, but only marks a slowing down, the reaction continuing at a reduced rate until the end. When the diastase is heated in solution above 60° its action weakened and an alteration is produced in the enzyme molecule, this alteration being assumed by the production of *d*- glucose when it acts on starch paste. The amount of *d*- glucose formed depends on the temperature at which the diastase in solution is heated before adding to the starch paste, the maximum amount being obtained when the solution has been previously heated at 68°–70° for about 20 minutes. The amount of *d*- glucose formed in any case does not exceed about 12 p.c. of the total hydrolytic products.

In 1903 Brown and Millar showed that the so-called stable dextrin, one of the hydrolysation products of starch by diastase, is converted by the further action of diastase into about equal parts of *d*- glucose and maltose.

This was confirmed by Ling and Baker.

In 1904, following on these results, came the new theories brought forward by Maquenne and Roux on the structure of the starch granule, and the discovery by Fernbach and Wolff of the enzyme termed amylocoagulose. These workers formed the opinion that when starch is acted on by diastase the maltose is produced from that portion of the starch granule they termed amylose, and that the residual unsaccharifiable dextrin comes from the amylopectin. A comparison of the action of malt extract at 50° on starch paste and a solution of pure amylose, gave results as follows:—

	Percentage of maltose on original starch substances	
	Starch paste	Amylose
5 minutes .	66·7 p.c.	94·4 p.c.
1 hour . .	79·0 ,,	99·7 ,,
2 hours . .	81·1 ,,	100·1 ,,
3 ,, . .	82·0 ,,	101·4 ,,
28 ,, . .	91·8 ,,	104·2 ,,

The apparent halt in the reaction in the case of starch paste when about 80 p.c. of maltose is formed is explained on the assumption that the hydrolysis of the amylose is then complete.

In 1906 Roux (Compt. rend. 1906, 142, 95), after further experiments with starch pastes of other starches, prepared at 100°, came to the conclusion that they were similar to potato starch in being composed of amylose and amylopectin. He found that they all tended to give the same dextrin and maltose proportions when acted upon with diastase.

In the same year, Roux, in conjunction with Maquenne (Compt. rend. 1906, 142, 124), found that when the alkalinity of starch paste was made exactly neutral to methyl orange with decinormal sulphuric acid, and the malt extract neutralised to the extent of one-third or two-fifths, saccharification proceeded more rapidly, and the yield of maltose showed a large increase.

Fernbach pointed out that malt extract is acid to phenol pthalein and alkaline to methyl orange, as if it contained a mixture of primary and secondary alkali phosphates, the optimum reaction for saccharification being neutrality to methyl orange.

In conjunction with Wolff, Fernbach showed that natural starches were similar in this respect to malt extract, and they found that if starch paste and malt extract be rendered exactly neutral to methyl orange, practically the whole of the starch is converted into maltose by the malt extract.

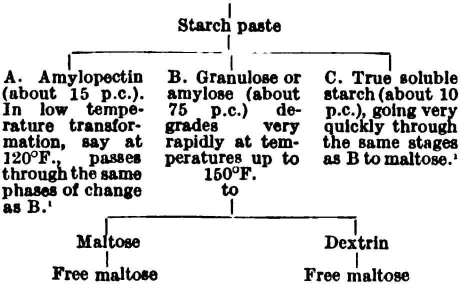
They came to the conclusion that the transformation of starch by diastase, if allowed sufficient time, will attain the theoretical limit of maltose production, and that the slackening observed in the later stages is due to the dilution of hydrolysable matter, and not to failure of the diastase. Solutions of the residual dextrins separated from an advanced transformation were found to be still susceptible to diastatic action.

Maquenne and Roux (Compt. rend. 1906) practically uphold these observations regarding saccharification, but consider that the reaction has two distinct phases, the first one of extreme rapidity, corresponding to the conversion of 70–80 p.c. of the starch into maltose, the second, a very slow one extending over several days.

In 1907 Van Laer (Bull. Soc. chim. 1907, 21, 8) discussed the later work on starch transformation, and accepted Maquenne and Roux's amylose and amylopectin hypothesis, but did not agree that the earlier work had been controverted, but rather had been extended. In starch conversions carried on at temperatures below 60°, the amylose may be regarded as being converted very rapidly into maltose with the producton of dextrins, the stable dextrin remaining being derived from the amylopectin. At temperatures above 60° dextrins are produced from the amylose of quite a different type, which are easily saccharifiable by malt diastase and correspond with the maltodextrin of Brown and Morris.

We must conclude, therefore, that from starch transformation with malt extract carried on at high temperatures we obtain mixtures of both kinds of dextrins, the complexity of which the older investigators ascribed to the modification of the action of diastase by heat, but which the more recent investigators attribute to the heterogeneous nature of the starch granule itself.

In 1911 Matthews and Lott (J. Inst. Brewing, 1911, 17, 219–266), as the result of a long series of experiments, practically endorse the views expressed by Maquenne in 1908 (*see* p. 152) on the structure of the starch granule, but find that experiments with potato starch do not exactly represent what happens with barley and malt starch when acted upon with diastase, but the relationship as to kind of products holds. Discussing dextrin they question whether really stable dextrin exists. Any so-called stable dextrin has its origin in the amylopectin, the part of the starch which requires liquefaction before transformation, any delay or injury to this action resulting in the production of very difficultly degradable dextrin. The weight of evidence appears to be entirely against the maltodextrin theory, but the proportions of combined maltose and dextrin in bodies of this character found in starch transformations mark them as ordinary products of change and representative of an intermediate state. The theory is that there is a stage in starch transformation where the whole of the readily transformable matter is present as a body degradable by successive stages to maltose. The change is represented as follows :—



Granular starch

Starch paste

A. Amylopectin (about 15 p.c.). In low temperature transformation, say at 120°F., passes through the same phases of change as B.[1]

B. Granulose or amylose (about 75 p.c.) degrades very rapidly at temperatures up to 150°F. to

C. True soluble starch (about 10 p.c.), going very quickly through the same stages as B to maltose.[1]

Maltose

Free maltose

Dextrin

Free maltose

Perhaps it is as well to call attention here to the fact that most of the work mentioned above has been carried out with carefully purified potato starch, but it has been ascertained that similar experiments made with widely differing starches—such as maize, rice, wheat, arrowroot, sago, barley, and various other starches—practically yield the same analytical results when acted upon in the form of paste by diastase, but it has been found that the same starches differ materially from one another when the unbroken granules are acted upon in the cold, as will be seen from the following table by Lintner (Brauer und Malzkalendar, 1890, 83)[1] :—

Table X.—*Action of Diastase on Ungelatinised Starch.*

Starch from	Percentage dissolved by 4 hours' contact at the undermentioned temperature				Gelatinisation temps.
	122°F.	131°F.	140°F.	149°F.	
					°F.
Potato starch	0·13	5·03	52·67	90·34	149
Rice "	6·58	9·68	19·68	31·14	158–167
Barley "	12·13	53·30	92·81	96·24	176
Green malt "	29·70	58·56	92·13	96·26	185
Cured " "	13·07	56·02	91·07	93·62	176
Wheat "	—	62·23	91·08	94·58	167–176
Maize "	2·70	—	18·50	54·60	158–167
Rye "	25·2	—	93·70	94·50	176
Oat "	9·40	48·50	92·50	93·40	185

All the known digestive ferments belong to the class of soluble or unorganised ferments, and of these only two appear to have any very marked action upon starch—the diastases of the saliva and of the pancreatic juice. The action of these diastases upon raw starch and upon starch paste is very similar to that exercised by the diastase of malt, with the exception that in addition to dextrin and maltose, dextrose is also formed, through the hydrolysis of the maltose by these ferments, the action on raw starches varying according to the kind of starch acted upon (*see* Roberts, Digestive Ferments ; Church, Food Grains of India ; Bell, Chemistry of Foods ; Brown and Heron, Proc. Roy. Soc. 1880, 393 ; Chittenden and Cummins, Chem. News, 51, 256 ; Chittenden and Smith, *ibid.* 53, 109).

16. *Action of bacteria.* According to Fitz (Ber. 10, 276 ; 11, 42), starch yields by fermentation with a *Schizomycetes* (*Bacillus butylicus*, *Bacillus subtilis*) 35 p.c. of butyric acid and 9 p.c. of acetic acid, together with a small quantity of succinic acid. Inulin appears to yield the same products.

By the action of certain organisms, starch is rendered capable of being converted into dextrin and maltose, and eventually into alcohol. In this way the Indians of South America make an alcoholic liquor called *chicha* by the fermentation of the starch of maize. The grain is first allowed to soak for from 4 to 6 hours to soften it and afterwards fermented. The fermentation is due in the first instance to the presence of a minute organism, situated on the epidermis of the grain ; this secretes a diastase, which either produces or aids further fermentation (Marcano, Compt. rend. 95, 856).

Gayon and Dubourg (*ibid.* 103, 885) mention a species of mucor which has the power of converting dextrin and starch into sugar, and then fermenting the sugar.

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[1] There is some evidence that a little dextrose may sometimes be formed.

[1] *V.* also Die Stärkenenbildenen Fermente f. Baranetzky 1878, and Brown and Morris, Chem. Soc. Trans. 57, 510.

Bacillus suavolens converts starch gradually into dextrin and glucose, with formation of alcohol, aldehyde, formic, acetic, and butyric acids, &c. (Sclavo and Gosio, Arch. ital. Biol. 14).

Villiers (Compt. rend. 112, 435 and 536) finds that the addition of a pure cultivation of *Bacillus amylobacter* to a 5 p.c. starch paste causes complete liquefaction in 24 hours, and on allowing the fermentation to continue some time the liquid no longer gives a blue colouration with iodine, the products of the change being almost exclusively dextrins, no maltose or dextrose being found to be present, from which he concludes that the organism converts starch directly into dextrin without the intervention of any diastase secreted by the ferment.

Perdrix (Ann. Inst. Pasteur, 1891, No. 5) has separated from Paris water a bacillus, *B. amylozymicus*, which ferments starch with production of dextrin, glucose, carbon dioxide, ethyl and amyl alcohols, acetic and butyric acids. A somewhat similar change is effected by the bacillus of malignant œdema (Kerry and Fraenkel, Monatsh. 12, 350).

MANUFACTURE OF STARCH.

17. *General considerations.* In growing various starch-producing plants for manufacturing purposes, the following facts must be taken into account: 1. The average percentage of starch contained in the root, tuber, or grain; 2, the yield per acre; and 3, the amount of starch yielded per acre. Thus, although the potato at best contains only 20 p.c. of starch; wheat, on the other hand, contains 55 p.c.; nevertheless the total amount of starch per acre is in favour of the potato, in the proportion of 2 to 1, since one acre of ground on the average produces 12,994 lbs. of potatos, containing 2598 lbs. of starch, as against 1860 lbs. of wheat, containing 1023 lbs. of starch.

Again, different varieties of the same species of plant will show very marked differences in the quantity of starch which they yield. For instance, the potato, as ordinarily consumed as food in this country, contains only about 13 p.c. of starch, but in Germany, where the potato is cultivated for starch production, by means of careful selection and suitable manuring the percentage of starch has been raised to as much as 20 p.c., and in some instances as great a yield as 24 p.c. has been obtained. The yield of starch is also affected by the age of the raw material, conditions of harvesting, and exposure to heat or cold during storage.

It has been found that over-ripe potatos contain less starch than others, the loss being from 3·18 to 9·88 p.c. on 100 of starch (Kramer, Bied. Zentr. 1881, 717).

A sample of barley, which had been exposed to bad weather for a fortnight, and had sprouted, was found to have lost an appreciable amount of starch, that in normal barley being 64·1, whilst that in the sprouted grain was only 57·9 p.c.

Diseased potatos contain considerably less starch than sound ones, owing to its conversion into sugar by the fungus which attacks them, those tubers which are grown with the aid of highly-nitrogenous manures being more susceptible to the disease than those which are grown under ordinary conditions (Gilbert, Agr. Students' Gazette, 4, pt. 2). Exposure to extreme cold tends to diminish the amount of starch in potatos, the generally-accepted idea being that by the freezing a portion of the starch is converted into sugar.

On the other hand, although the materials may be all that is desired, the yield of starch may be low, from causes due to carelessness in the processes of manufacture, such as insufficient washing or defective machinery, &c.

The raw materials almost exclusively employed in Europe and North America for the preparation of starch therefrom are wheat, potatos, maize, and rice. Wheat was very generally used at one time, but has now been almost entirely replaced by the other substances. Potatos are very largely employed on the Continent, rice principally in England, and maize almost universally in America.

The manufacture of starch may be classed under three heads.

1. For manufacturing purposes generally, such as the sizing of paper and of cotton goods, the dressing of cloth, the thickening of mordants and colours in calico-printing, the preparation of British gums, of white glucose syrups, &c.

2. For laundry purposes.

3. For edible purposes, either by itself, as in the preparation of cornflours, arrowroot, tapioca, &c., or in conjunction with other substances in the preparation of sauces, macaroni, semolinas, &c.

Starch was extracted from wheat and barley by the ancient Egyptians, Greeks, and Romans. It was called ἄμυλον by the Greeks, from the circumstance of its not having to be prepared by the action of grinding in mills like other farinaceous substances, whence the Latin *amylum*. Very little, however, appears to have been known about its history or composition until the beginning of the 18th century.

18. *Manufacture of starch from wheat.* The different methods of preparing starch from wheat are:

I. By fermentation, known as the old or sour process.

II. Without fermentation, or Martin's process.

I. Fermentation process. For the old method the wheat is used either whole or ground, but most frequently whole.

Where the whole corn is employed, the wheat is steeped in soft water for some days, until it becomes swollen and so soft as to be easily crushed between the fingers; the water being changed frequently, so as to ensure, at the same time, a thorough washing of the grain. The swollen corn is now transferred to bags, and placed in a wooden chest or flat tub, where it is exposed to strong pressure. By this means the grains are crushed, and the water, which is rendered milky by the starch, is drawn off by means of a tap; fresh water is poured in, and the pressure repeated until all or nearly all of the starch is extracted. Instead of putting the swollen grain in bags, it may be passed from a hopper between two wooden cylinders revolvin in opposite directions, or between one or two cylinders revolving upon a horizontal stone having a rim, to a cistern; by this means the swollen corn is readily crushed and the starchy liquor in the cistern separated by elutriation with successive quantities of water.

The milky liquor containing the starch is next run into cisterns, where it is allowed to remain for a period of from 10 to 30 days, according to the temperature of the surrounding atmosphere, during which time it undergoes fermentation, in order to accelerate which some of the sour liquor from a previous fermentation is added.

By this means the starch granules become completely freed from the glutinous envelopes containing them in the grain, the gluten becomes more or less decomposed and softened, and partially dissolved in the acids formed during the process, and completely loses its sticky elastic properties.

During the earlier stages of the fermentation the ready-formed sugars of the grain, as well as dextrin resulting from the action of the diastase on any broken starch granules, become converted into alcohol, which later on is changed into acetic acid; after a few days lactic, butyric, and other fermentations are set up, and allowed to proceed until the process is considered sufficiently far advanced to allow of the starch granules being easily separated in a state of comparative purity. As a rule, actual putrefaction, as shown by the evolution of stinking gases, should be avoided as much as possible, and the fermenting mass should always have an agreeable vinous smell. During the process it is necessary to agitate the mass throughout once or twice a day, in order to equalise the fermentation as much as possible.

As soon as the fermentation is considered to have progressed far enough the supernatant liquor is drawn off and fresh water run in, the whole well stirred up, allowed to settle, and the surface liquor drawn off. This washing is repeated as long as any perceptible colour is imparted to the water; after the last deposition and decantation, the starch will be found to have settled down in layers of varying purity, the topmost one containing the most gluten and albumen. These different layers are now taken up with a wooden shovel, and transferred to separate cisterns, where they are agitated with water and then passed through fine sieves. After the starch has again settled down, the clean water is drawn off, any impurity that may be on the top separated, and set aside to be washed up with the next batch; the underlying portion agitated again with fresh water, and purified by settling and decantation, this being repeated as often as may be deemed necessary.

It is then shovelled into wooden boxes about 4 feet long, 12 inches broad, and 6 inches deep, perforated throughout and lined with thin canvas; this is termed 'boxing.' When it has drained and dried into a compact mass, it is turned out by inverting the box upon a clean table where it is cut up into pieces 4 or 5 inches square; these are then set upon half-burned bricks, which by nature of their porosity absorb the moisture from the starch, so that the under surface of the blocks may not become hard and horny.

When sufficiently dried upon these bricks, the blocks of starch are put into a stove and left there until tolerably dry; they are then removed to a table, where all the sides are carefully scraped with a knife, next packed up in the paper in which they are sold, returned to the stove, and subjected to a gentle heat for some days, previous to being sent into the market.

II. Martin's process. In this process flour is employed in preference to the whole or crushed grain. It is kneaded into a stiff dough with water, exactly as for bread-making, and allowed to remain in that state until every part becomes thoroughly saturated with moisture. This requires 25 minutes in summer and about an hour in winter. For the separation of the starch from the gluten an apparatus is employed, consisting of two troughs which are similar to each other, and which may be of any convenient length. Within each of these troughs there is a rectangular frame, which is caused to move to and fro within the trough by a crank axis and connecting rod, the crank of one trough being set opposite to that of the other.

Each of the frames carries the bearings of four or other convenient number of grooved rollers. At the bottom of each of the troughs there are openings at intervals covered with wire gauze; at the ends of each trough are applied spring buffing apparatus. Below the troughs is an inclined sieve of fine wire gauze, and below it an inclined shoot, down which the fluid which passes the sieve flows, and from it into any suitable receiving vessel, where the starch is allowed to settle; above each trough there is a perforated pipe, through which the numerous jets of water flow on to the dough introduced into the trough, and which serves to wash away the starch from the gluten.

The dough which is to have the starch separated from the gluten is formed into small balls, and placed in the troughs between the rollers. The frame carrying the rollers is caused to reciprocate, a constant spray of water being allowed to flow over the dough at the same time, by which means the starch is washed out and separated from the gluten; the milky liquor flows through the openings in the bottom of the trough on to the inclined sieve, and thence by means of the shoot to a suitable receiving vessel. Should any particles of gluten pass through the openings, they pass along the inclined sieve, and are received in a vessel. After the dough has been subjected for a sufficient length of time to the action of the rollers, it consists for the most part of gluten, and is placed between the ends of the frames and the buffing apparatus, where it is beaten for several minutes, and can then be used for any purpose to which it is applicable.

The purification of the starch obtained in this way may be effected in the usual manner, by successive washings and decantations as in the fermentation process, or by the inclined plane method described below under potato starch. Subsequently, Martin introduced the following process for the purification of the crude starch, whereby a better product is obtained than is possible by mere washing with water. This consists in treating the impure starch with a weak solution of sodium hydroxide, sp.gr. 1·013, in sufficient quantity to turn red litmus paper blue, after the deposit has been well roused up. The mass is then allowed to stand for two hours, during which time the gluten swells up, and becomes partly dissolved. A considerable quantity of water is then added, and the whole thrown on to a No. 200 sieve, which retains the swollen gluten and allows the starch to pass through; the starch is then run on to the inclined plane as before. Almost the whole of the starch is by this means obtained as a first product, whilst with simple washing about 25 p.c. is produced in an impure, unmarketable form.

On the average, there is obtained from a sack of flour about 110 lbs. of moist gluten and about 220 lbs. of dry starch.

19. ***Manufacture of starch from potatos.*** At one time the manufacture of starch from potatos was carried on to a certain extent in Great Britain as well as in Ireland, the first published specification relating to starch being taken out as far back as the year 1717 by Newton, Nowell, Clark, and Joynes, for 'a way or method to make starch of and from the roots called by the name of potatoes,' but its development has been considerably checked by the potato disease, and is now entirely replaced by starch from rice.

In France and Germany, however, where much more attention has been directed to the growth of the potato as a starch-producer, the manufacture of fecula or starch from this source has attained very considerable dimensions and large quantities of potato starch are imported yearly from those countries.

On the Continent the manufacture of potato starch, for an account of which the writer is much indebted to Payen's Chimie Industrielle, includes the following operations—steeping, washing, separation of stones, rasping, straining, settling, removal of the starch, purification, second straining, washing, draining, and drying in the air or in a centrifugal machine, drying in an oven, packing.

Steeping. Potatos which are grown in tough clay or loam are covered with adherent earth, which clings so tenaciously to them as not to be removed by simple washing; they are therefore allowed to soak for several hours in a large vat containing water.

Washing. In France this operation is carried on as follows:—An apparatus called the washing drum (Fig. 1) is used, consisting of a hollow revolving cylinder *b*, formed of wood or iron bands, ½–1½ inches wide, and laid longitudinally from one end to the other, the distance between each being about ¾ inch, so as to allow of the escape of the dirt, sand, and stones, whilst the tubers are retained. The cylinder, which is slightly inclined, is immersed to half its diameter in water in the trough *c*, wherein it revolves at the rate of about fifteen revolutions per minute, and by which means the potatos are kept in continual motion, rubbing against and being rubbed by the sides of the cylinder. From the sides of the trough spring the boards *g*, slanting to the upper part of the cylinder, so as to prevent splashing of the water. The cylinder is worked by a band from the main shaft, passing over the wheel *f*. The potatos are fed into the hopper at *a*, and are thrown out at the opposite end, where, falling down the inclined plane *d*, they are conducted to the stone catcher (Fig. 2). This apparatus consists of a semi-cylindrical sloping trough, filled with water to the level A. In the trough is a shaft D, furnished with arms placed spirally (Figs. 3 and 4), and which by means of the cogwheel E is rotated by the driving wheel F. The potatos being fed in at A, are rubbed upon one another by the arms and repeatedly dipped in the water, so that the remainder of the dirt and all stones and sand is washed off, and, the heavier particles sinking to

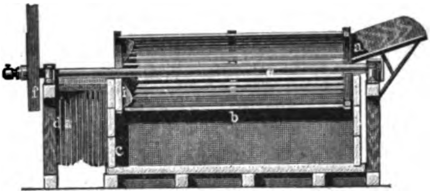


FIG. 1.

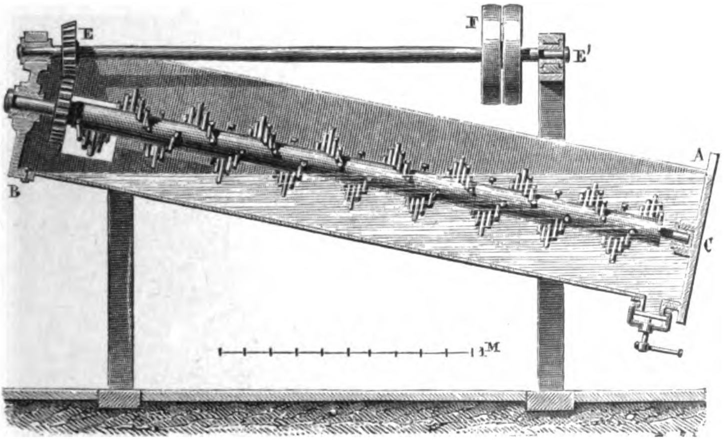


FIG. 2.

the bottom, are removed from time to time through the opening C. The potatos are carried forward by the action of the spiral until they reach the upper end of the trough, over which they fall into the hopper of the rasping machine.

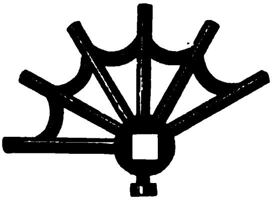


FIG. 3.

FIG. 4.

In the German factories the above operations are carried on at one and the same time, the trough in which the washing drum is placed being divided into two unequal parts, the larger one *d* for the washing drum, and the other *e* for the stone catcher; as shown in Figs. 5 and 6, the potatos are introduced into the smaller division *e*, and are drawn forward and kept in incessant motion by six or eight large iron arms *gg*, arranged spirally on a prolongation of the shaft of the washing drum *ab*. The stones, sand, &c., are drawn off at intervals through the openings *i* and *h*. The potatos thus reach the washing drum previously washed and freed from stones, from which they pass through *kk* to the rasping machine.

By means of this the tubers are reduced to a pulp, and the cells containing the starch are ruptured; and the more completely this is done the greater the amount of starch obtained, since it is only the starch from the cells which are actually ruptured that can be extracted, whilst all that remains in closed cells represents so much loss to the manufacturer. For this purpose Champonnois' rasper is generally considered the best, and is shown in Figs. 7 and 8. It consists of a hollow cylinder furnished with saw blades on its inner surface, against which the potatos are made to rub. The case A of the cylinder is seen in Fig. 8, with the rasper inside. This is so arranged that from one to four saw blades lie between thin steel bands, at an interval of from $\frac{1}{30}$–$\frac{1}{25}$ of an inch apart, and between each group is a space through which the pulp as it is formed can pass. This arrangement is shown in Figs. 9 and 10.

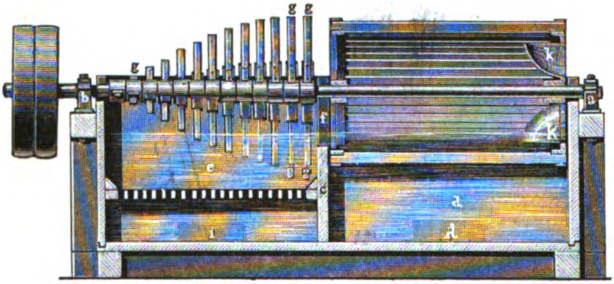


FIG. 5.

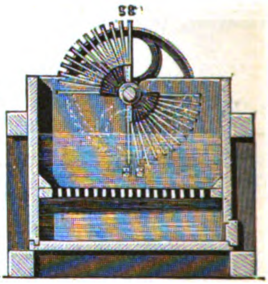


FIG. 6.

FIG. 7.

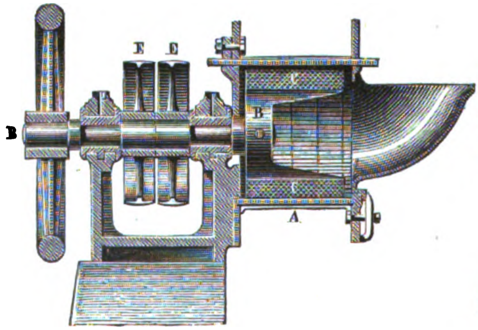
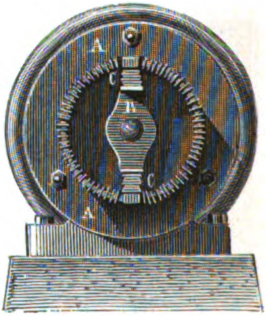


FIG. 8.



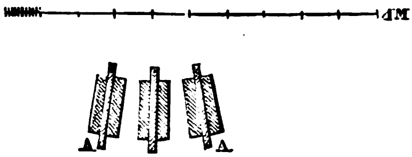


FIG. 9.

FIG. 10.

In the axis of the rasping cylinder is a shaft BB, making 800 to 1,000 revolutions per minute, by means of a band from the main shaft applied to the driving-wheels EB, and regulated by a fly-wheel. At the other end of the shaft, within the drum, is a strong fork-shaped scoop. The potatos, falling through a side opening, are seized by the scoop, and pressed forcibly against the saw blades CC in the cylinder. Water, being admitted into the interior, is driven by centrifugal force against the sides of the cylinder, and makes its way through the interstices, carrying with it the potato pulp, which passes away through a pipe underneath. The teeth of the saw blades are very short, projecting one-fifth of an inch from the drum. They require reversing twice a day, and after two days' use need to be re-filed. As much as thirteen tons of potatos can be rasped by this machine in ten working hours, whilst the yield of starch from a given quantity of potatos is considerably increased.

The pulp thus obtained is a mixture of starch and fibre. In order to separate one from the other the pulp is washed with water upon brass-wire sieves of different degrees of fineness, which allow the starch granules to pass through with the liquid and retain the coarser portions of the fibre. Several forms of apparatus have been devised for this purpose, the principal objects aimed at being uninterrupted working, as complete exhaustion as possible of the pulp within the smallest space, and economy of wash water. Fig. 11 shows a longitudinal section of Huck and Stoltz's machine. This consists of three cylinders A, B, C, of different diameters. The case of the first is formed of a wire sieve, 25 meshes to the inch. The pulp from the rasper is run in through the funnel *a*. Within this cylinder is another, *bb*, formed of perforated metal plate into which water flows through the pipe *a''*, and is distributed uniformly upon the potato pulp in A by means of the perforations in *bb* from A. After parting with the greater part of its starch the pulp is gradually brought forward into the second cylinder B, which is covered with sheet copper. The pulp is here worked about with a T-shaped iron fastened to the shaft DD′, which is rotated by the driving wheel G in an opposite direction to the cylinder; from here it is carried forward to the third cylinder, which is covered with wire tissue, 35 meshes to the inch, where it meets with a fresh spray of water coming through the perforated pipe *dd* from *a'''*. Whilst in the cylinders A and C the pulp undergoes a continual working with brushes, which, like the agitator in B, are connected with the shaft DD′. These three cylinders revolve at the rate of 22 revolutions per minute; whilst the agitator in B makes 35 in the same time. The starchy liquid flowing from A and C is collected in the trough K, and runs from thence into the sieve cylinder HH′, which is covered with wire gauze, 50 meshes to the inch. Here any fibrous pulp which may have passed through the other sieves is retained; whilst the water containing the separated starch is run off along the trough L into the settling vats. The coarse pulp as it is pushed out of the cylinders falls into the receivers MM′ underneath. In order to prevent the clogging of the sieves, a fine stream of water is thrown upon them during working from pipes running parallel with their axis.

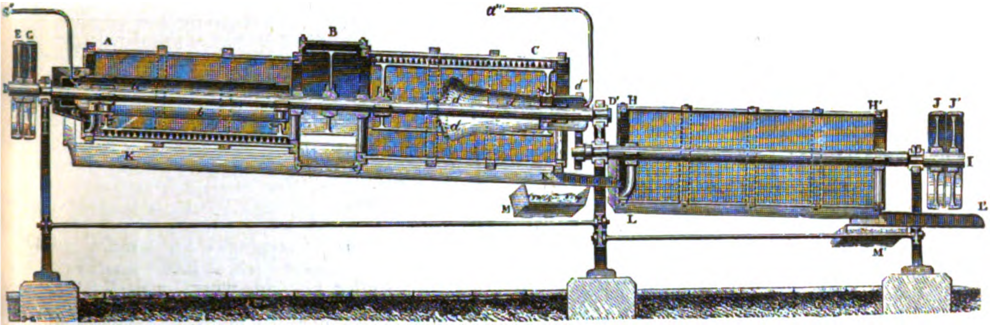


FIG. 11.

A modification of the above apparatus, by means of which considerably less water is required, and which is suitable for localities where water is more or less scarce, is shown in Fig. 12.

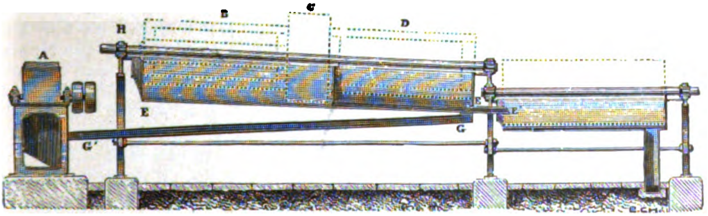


FIG. 12.

The pulp coming from the rasper A is raised by means of a centrifugal pump into the first cylinder B, where it gives up by far the greater part of its starch. The strained liquor from this cylinder is not joined with that from the other cylinders, but runs straight away into the purification vessel. The liquor from the mixing cylinder C and the other sieve cylinder D, containing comparatively but little starch, is carried by the pipe GG′ back to the rasper, where it is used instead of clean water for the thinning of the pulp.

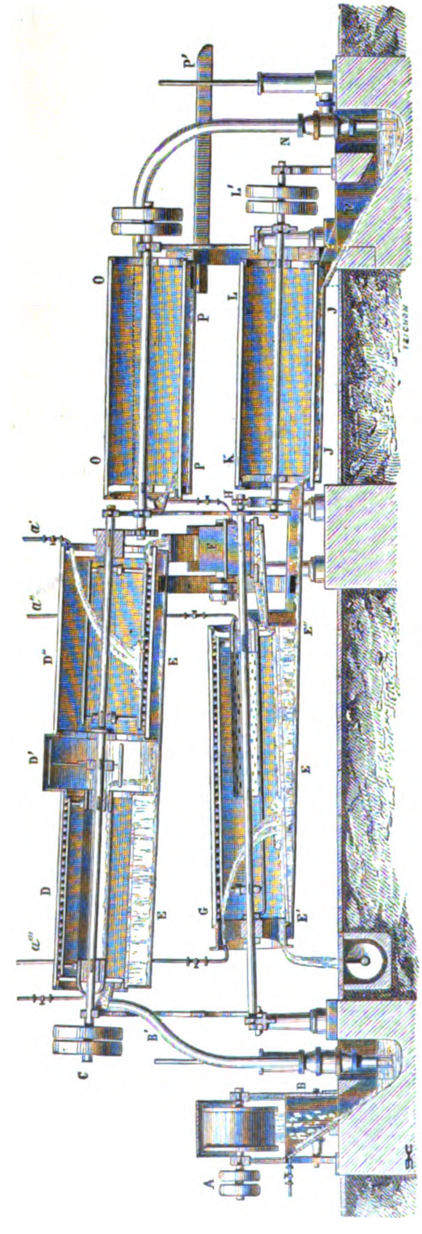


FIG. 13.

In some factories, by means of a modification of the apparatus just described, a second working of the pulp is effected, and a larger yield of starch thereby obtained. This is shown in Fig. 13. The pulp, thinned with water, falls from the rasper A into a small cistern, from which it is raised by the pump B, through the pipe B′, into the sieve and mixing cylinders D, D′, D″, and in the latter washed by a stream of water a'. The pulp rejected from D″ falls into the hopper of a second rasper, where it is rubbed between two cylinders F rotating in opposite directions; from thence it flows into the sieve G, where it meets with more water from a''', and, being washed, falls into a trough, along which it is pushed by an Archimedean screw.

The starchy liquid from D falls into the trough E, that from G into E′, and both united fall into the first purifier KL, thence into the trough J, into the cistern M, from whence it is raised by the pump to the second purifier O, where the last portions of fibre remain, whence by means of the trough P the liquor containing the nearly pure starch passes to the purification apparatus. In the smaller factories this is generally accomplished by means of settling vats.

In addition to rasping, a great many manufacturers are accustomed of late years to grind the pulp after rasping, whereby a slightly increased yield of starch is obtained. The following figures, calculated on the starch worked, show a comparison between the yield obtained when a rasping machine only is employed, and when, in addition thereto, grinding is carried on as well.

Obtained in form of green starch	Without grinding	With grinding
Experiment A. . .	81·8	87·4
Experiment B. . .	76·3	85·5

Various forms of machines for carrying on the rasping and grating processes simultaneously have been constructed during the last few years.

The starchy liquor as it comes from the sieves generally contains some sand, which was not separated during the washing of the potatos, and was too fine to be retained by the sieves. It is therefore run into a large vat and vigorously stirred so as to bring all the starch into suspension, and, before it has had time to settle, is siphoned off into another large vat, where it is allowed to stand for four hours, during which time the starch settles on the bottom. The sand, by reason of its greater specific gravity, sinks rapidly to the bottom, and remains in the first vat. The lower part of the sediment deposited in the second vat consists of pure starch, covered by a greyish layer, consisting of fine fibres that have passed through the sieves. The supernatant liquor having been run off, this impure mass is scraped off as clean as possible with an iron scraper. This impure starch is agitated with fresh water, passed through a very fine sieve, and allowed to rest for some time, until a further amount of white starch falls out, when the same operation is repeated.

The purified starch is again agitated with water, passed through a silk or wire sieve, 90 meshes to the inch, and again allowed to settle, the liquor decanted off, the surface of the starch scraped, and finally, if the mass be pure enough and of sufficient consistence, divided into lumps and placed to dry.

Sometimes the starch, deprived of its supernatant brownish deposit, is purified by being placed in a slightly sloping flat-sided trough about 22 feet long and 3 feet wide. Below this is a second trough, inclined in the opposite direction; and below this a third, inclined like the first. A spray of water from a very fine rose falls upon the starch, which is placed just beneath it at the top end of trough No. 1, and at the same time is kept constantly stirred. The water gradually washes everything forward with it, and while slowly flowing along the troughs the starch is gradually deposited; whilst the lighter fibrous matter remains in suspension, and passes with very little starch into vats underneath. The starch obtained in this way is added to that purified in the first settling vat, and is then ready for draining.

In large factories the settling vats have been entirely superseded by the inclined plane; this consists of a series of three wooden troughs, Fig. 14, 3½ feet wide and about 30 yards long, each having a fall of 1 to 1½ in 1,000. The third plane or trough rests on the ground and empties into the vat G. The second and first are affixed to wooden supports as shown. The starchy liquor, as it comes from the cylinder sieves, enters the first inclined plane at A, flows along in the direction AB, and thence along CD to F, the flow being regulated at will by means of the screw valves at B and D. The greater part of the starch is deposited in the first plane, from which it is removed once a day. The starch from the second plane, on which considerably less is deposited, is removed twice a week; and that from the third once a week. The liquor, containing very little starch, flows into vat G, or generally into a series of vats, whereby any starch that may still remain in the wash water is collected.

The starch thus deposited on these inclined planes is sufficiently pure for most purposes to be sent at once to market; but, as it is still contaminated to a slight extent with potato sap, it is advisable to wash it once or more in the usual settling vat in order to purify it completely.

Drying. The starch is taken from the planes or settling vats in the form of a very thick mud or sludge, from which the greater portion of the water may be removed by centrifugal action, by drying in the air or in ovens.

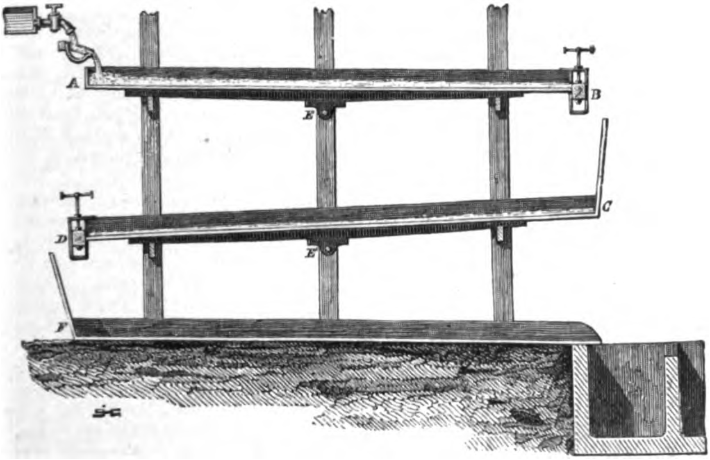


FIG. 14.

In the drying of starch by centrifugal action the same form of apparatus is used as in the manufacture of sugar, but as the starch mud is so thick as to render it incapable of being properly distributed on the sides of the machine, a quantity of water is mixed up with it to bring it into a sufficiently thin paste that will flow into the apparatus whilst it is in motion. It is then flung against the circumference of the machine, the water flies off, and the starch lies as a compact mass round the sides of the cylinder. Advantage has been taken of centrifugal action for the purification, as well as for the drying of starch at the same time, by Fesca, of Berlin. When the impure starch liquor is introduced into the machine, the densest and heaviest portion—and consequently the purest starch—is driven first against the sides of the cylinder. The fibrous portion remains longer suspended, and is deposited as a layer upon the surface of the pure starch, from which it is easily removed.

For many purposes—such as the manufacture of dextrin and glucose, &c.—the starch, as it comes from the centrifugal machine, and containing from 35 to 40 p.c. of water, needs no further desiccation, and is known in commerce as green starch.

In factories where a centrifugal machine is not used, the water is removed as much as possible from the starch before proceeding with the drying. Accordingly, as soon as the starch is considered sufficiently purified, it is dug out of the settling vats and transferred to perforated boxes, lined with clean linen, and set aside for some time to drain, during which time it acquires sufficient hardness to enable it to retain the shape of the box, and as soon as ever this takes place the box is inverted upon a dry porous slab, generally of plaster-of-Paris, which abstracts a further amount of moisture, so that it arrives at the state of green starch. It is now sufficiently solid to be removed to the drying room, on either side of which a series of shelves, formed of bars of wood placed at a distance of about one inch apart, are ranged in tiers one above the other, through which a current of air is made to pass freely by means of louvre boards or venetian ventilators. On these shelves the blocks of starch are placed, and allowed to remain for six or eight weeks, until sufficiently dried. One great drawback to this method is the exposure of the starch to any dust that may be floating about in dry weather, as well as the possibility of the moist starch becoming frozen in cold weather. The latter may be obviated by introducing heated air into the drying-room, and the dust precluded by shutting up all the windows—in fact, by practically converting the room into an oven. The starch dried in this manner is known as 'hurdle starch.'

The best quality, termed superior, which is used for the manufacture of starch sugar and dextrin, is singularly white, glossy and pure, and consists of large grains, being the first to deposit in the settling tanks. The deposits become lower in quality in succession. The gloss of starch depends on the size of the grain, the larger the grains the better the gloss, and the determination of the diameter of the grains by means of the microscope forms a good test for this starch.

A superior article consists of grains having a diameter 35·5μ, ordinary prima 32·5μ, prima seconds 21·0μ and inferior kinds 17 to 12·5μ. Considerable importance is also attached to the amount of impurity present, such as coal dust, potato skin, soot, sand, iron particles from wheels, algæ from water, particles of wood, &c. The amount is ascertained by smoothing a sample on white paper, and counting the particles in a square cm. Superior starch contains 15 to 30 particles, average samples 27–170, while inferior kinds contain as many as 800 upon 1 sq. cm.

20. *Manufacture of starch from rice.* Although no other starch-producing material is so rich in this substance as rice—containing, as it does, over 80 p.c. of starch—nevertheless, the cells and the starch granules contained in them are so intimately connected together by a small but very resisting quantity of gluten that their separation cannot be effected by a simple crushing and washing, as in the case of potatos, or by the old system of fermentation, as in the case of wheat and flour, and hence resort must always be had to chemical agents, alkalis or acids, to effect this object.

Since rice starch, on account of the smallness of its granules, possesses a greater firmness, and in practical operations gives a much higher lustre than wheat starch, it is much esteemed by laundresses, and preferred by them to any other, so that when the difficulties attending its successful preparation had been overcome, a great impetus was given to its manufacture in England, where it is at present carried on to a very large extent, and, being cheaper in this country than any other raw material, may be considered as a fairly remunerative business.

It need hardly be said that the value of any sample of rice for starch manufacture depends not only upon the amount and quality of the starch it contains, but on the percentage of gluten or protein matter as well, and on its degree of solubility in caustic soda solution.

The following analyses of rice from different countries show the relative amounts of these substances which are generally present in the matured grain :—

Analyses of rice.

——	Patna (Polson), cleaned	American (Jenkins), mean of 10 analyses	Japan (Kellner), mean of 10 analyses
Carbohydrates .	81·81	79·20	74·10
Proteids . .	7·22	7·40	6·13
Fat . . .	0·09	0·40	2·00
Fibre . .	0·18	0·20	4·00
Ash . . .	0·90	0·40	1·19
Water . .	9·80	12·40	12·58

The method of manufacture described by Jones (Eng. Pat. 1840, No. 8488)—and which is, with a few modifications, the one carried out at the present time in England—is as follows.

One hundred pounds of rice are placed in a tinned copper or stoneware vessel holding 50 gallons of a solution of sodium or potassium hydroxide, containing 200 grains of alkali per gallon of water; the mixture is well stirred and allowed to macerate for 24 hours, at the end of which time the liquor is siphoned off, and the rice well washed with twice as much cold water as there was of alkaline solution. The water is next poured off, and the grain placed upon sieves to drain, after which it is crushed or ground to flour with rollers or millstones. The flour is then passed through sieves by means of brushes, the coarser particles which do not pass through being returned to the mill to be reground and again sifted, until the whole is thus disposed of.

The flour thus obtained is again treated with alkali solution, one hundred pounds of the rice flour being added in small quantities at a time, to every hundred gallons of liquor. The whole is repeatedly stirred up during 24 hours, and then allowed to stand for about 70 hours to settle. The processes of this deposit takes place as follows: the first deposit consists of fibrous matters with little starch, followed by a deposit of the greater portion of the starch, the gluten and other matters remaining in solution in the alkaline liquor, which is siphoned off, and double as much water run on. The deposit is then well roused up with it, and the whole allowed to stand about an hour, during which time the matters other than starch subside, carrying with them a small portion of the starch, but leaving by far the greater bulk of it suspended in the liquor. This is drawn off, and passed through fine silk sieves. A further quantity of water is added to the deposit and agitated as before, and, after standing a short time again drawn off, and passed through sieves as before, this operation being repeated as often as necessary, until at length the whole of the starch is separated from the fibrous and other matters.

All these starchy liquors are then collected into one vessel and allowed to settle for about 70 hours, during which time the whole of the starch is deposited. The supernatant liquor is now drawn off, and the starch (blued if necessary) drained, dried, and finished in the usual way.

Several other patents for preparing starch from rice have been taken out by various manufacturers, the principal of which are the following :—

Berger's process (Eng. Pat. 9013, 1841).—By this method : 1. Starch is manufactured from rice by the application of an alkaline salt, *e.g.* sodium carbonate, whereby the gluten is dissolved or freed, so that the starch may be separated therefrom. The operations are in all respects analogous to those of Jones' process.

2. The rice is soaked in water and submitted to a process of fermentation ; or

3. The first and second processes are combined.

Colman's process (Eng. Pat. 2166, 1841).—1. Rice is mixed with the refuse from wheat or other grain in the proportion of fifteen pounds of the latter to every hundredweight of rice, and, the necessary quantity of water being added, the mass is allowed to ferment for 10 to 15 days, after which the starch is separated by washing and sifting as already described.

2. The rice is steeped in water for 4 days, then drained, and reduced to a pulp in a mill under a stream of water, collected in a reservoir, allowed to settle, and the water siphoned off.

The deposit is then agitated with a dilute solution of hydrochloric acid (about 2 p.c.) and allowed to stand for 5 days, being well stirred every 4 hours during that time, then allowed to settle for 18 hours, the clear liquor drawn off, and the operation repeated with a 0·5 p.c. acid solution. Finally, the deposit is washed with large quantities of water, passed through sieves, drained and dried in the usual way.

Rehe patented a process (Eng. Pat. 10359, 1884) according to which the rice is first submitted to a temperature of 160° to 180°F. before steeping, and afterwards macerated in soda lye (four pounds of soda to every hundredweight of rice), and the starch extracted in the usual manner later on.

Ransford introduced a process (Eng. Pat. 1853, 603), in which pressure is applied to the rice after it has undergone the steeping operation. The rice having been put into the steeping liquor, in a vessel capable of being closed down, is allowed to steep for some time. The vessel is then closed down tight and more liquor forced in by means of a pump, up to about 20 lbs. to the square inch ; this is continued for a short time, the liquor drawn off, and again pumped in. The liquor is then drawn off, and the rice further pressed so as to drive out as much gluten as possible, after which it is ground and treated in the usual way.

In Germany the manufacture of starch from rice has replaced wheaten starch to a large extent, and J. Berger, who appears to have given much attention to this subject, has published an interesting account of the process as carried out there at present (Chem Zeit. 14, 1440, 1571 ; 15, 843), an abstract of which is given below.

The raw material principally employed in Germany is obtained from rice-cleaning and polishing-mills, and consists of the broken grains. The percentage composition of various samples of this waste is given in the following table :—

—	East Indian rice			Russian rice	Egyptian rice	Persian rice
Water .	12·10	13·20	13·23	12·70	11·84	10·80
Starch .	76·25	73·90	77·44	75·81	78·30	73·20
Protein .	8·95	8·79	6·87	7·94	6·70	11·21
Fat .	0·42	0·71	0·35	0·40	—	0·75
Gum and sugar .	0·86	1·20	0·95	1·21	—	1·45
Fibre .	0·32	0·40	0·36	0·44	—	0·81
Ash .	1·10	1·80	0·80	1·45	1·16	1·78

Extraction. The operation for the extraction of starch is carried out in shallow tanks of 4–5 cm. capacity. The rice is piled on a perforated shelf fixed in the tank, and covered with soda lye of 0·5° to 1°Bé. The mixture is stirred a few times, and after about 18 hours the lye is run off and replaced by a fresh lot, which is allowed to remain for 12 hours, by which time the rice is, as a rule, sufficiently softened to be ground ; this is effected between millstones 1200–1400 mm. in diameter and 300–400 mm. thick, and making 120 to 140 revolutions per minute. Incomplete grinding must be avoided as much as possible, and therefore in most factories the rice is passed through two mills arranged side by side, so that the ground starch drops directly from the first into the second mill. During grinding, the rice is moistened with lye of the same strength as that used for softening, about 200 litres being required per 100 kilos. of rice. The starchy liquor flowing from the mill, and containing about 20 to 28 p.c. of solid matter, is carried up by suitable means to high-lying tanks, from whence it is distributed to the sieves and other apparatus.

Sieves. Rotating cylindrical sieves are almost invariably employed, and are constructed as follows : A shaft, 4–5 metres in length, is provided at intervals of 1 metre with three rods of equal length, arranged symmetrically at right angles to the shaft. The ends of these rods carry six wooden boards parallel to the shaft. The framework thus formed is covered with the finest silk gauze. The cylinder is so arranged that one end of it lies about 15 cm. higher than the other. The liquid to be strained is fed into the upper part of the apparatus. The starchy liquor, as it filters through, is collected in a wooden casing, which completely surrounds the cylinder, whilst the impurities remaining on the sieve pass along into a tank opposite the lower end of the cylinder. The shaft of the cylinder being hollow, and pierced with numerous holes, allows water to be forced through on to the sieves. By this means the walls of the cylinder are kept clean, and the passage of the impurities towards the lower end is facilitated. The starchy liquor passing through the sieves still contains much gluten, which may be separated in the manner described under *Potato starch*, either by means of settling tanks, or with the centrifugal machine.

Berger suggests many improvements in the above process. Great stress is laid upon the importance of the preliminary softening of the rice with a solution of caustic soda, as the precise action of caustic soda has been misunderstood by most rice-starch manufacturers, being generally regarded as a mere mechanical one instead of a distinctly chemical one, the caustic soda dissolving out the albuminous substance which cements the starch cells together, thus rendering them more amenable to the after-operations. This softening process should be carried out as quickly as possible, especially in warm weather, in order to prevent fermentation, the evil effects of which are to be seen in all the after-processes. It causes the mass to froth excessively in the grinding-mill, and renders centrifuging difficult, the starch not separating as it ought to do in a state of purity, but coming from the centrifugals in flabby lumps; and, for the same reason, it refuses to deposit in the settling tanks. The gluten assumes a slimy condition, and retains much starch. In order to obviate this, Berger recommends that the extraction and softening of the rice be effected by a continuous current of slightly stronger lye (1½°Bé.), as by this means the treatment is considerably shortened, and at the same time the action is rendered more energetic.

Another method proposed by Mack (Dingl. poly. J. 256, 35), and which has been successfully adopted in Germany, consists in blowing air under pressure through the mixture of rice and caustic soda in such quantities that the liquid assumes the appearance of boiling. For this purpose air enters through a series of small tubes into a tank provided with a false bottom, on which finely-ground rice is spread, the tank at the same time being filled with the caustic soda solution. After the operation is finished the liquor is run off, and the resulting rice starch allowed to drain. By this process the rice is said to soften quicker, and yields from 6 to 8 p.c. more of the finished product.

When the various processes are employed in the order given, the yield of starch of the first quality is about 60 p.c. (calculated as absolutely dry starch on the rice), whilst 7–10 p.c. are left in the various by-products, and may be recovered by repeated treatment.

The total yield in a properly conducted factory is about 85–90 p.c. of the starch contained in the rice.

Moulding the starch. Formerly this was almost exclusively done in wooden boxes with perforated bottoms covered with filtering cloth. The boxes are set up in rows, and the starch mixed with water or weak soda lye (0·1° to 0·3°Bé), being charged into the first box, overflows into the next, and so on. In order to make the water drain out more thoroughly, the boxes are repeatedly lifted from their supports and dropped again. After about 24 hours the blocks of starch, still containing 42–44 p.c. of water, are removed, and cut into rectangular pieces. Various forms of high-pressure filtering moulds are now employed, and with these the starch-milk used for filling must not exceed in sp.gr. 1·2–1·25, otherwise the finished product exhibits a rough fracture which detracts from its appearance.

Drying the starch. Blocks of starch, containing 40–45 p.c. of water, when dried, become covered with a yellow crust, owing to the separation of traces of dextrin, &c. This crust is about 10 mm. thick, and is cut off when the blocks are partially dry—*i.e.* contain 25–28 p.c. of water. The remaining starch may be now completely dried without any further development of yellow colour taking place. All attempts hitherto made to avoid this crust formation have failed. The crust constitutes about 20–30 p.c. of the total starch. The shavings are stirred up with water, centrifuged once, or filtered, and mixed with the subsequent batch of pure starch. Large masses of starch, when dried, fall into more or less irregular rod-like pieces, the size, shape, and smoothness of surface of which depend greatly on the rapidity of drying and the solidity of the blocks before drying, too rapid drying or too slow drying producing discoloured pieces which readily crumble during transit. The same thing happens when particles of fibre are present, the even fissures being prevented by their presence. Starch is generally coloured in order to hide its slightly yellow tint, ultramarine being usually employed for the purpose. The blocks after being planed and wrapped in paper, are kept for 2–3 days in the drying chamber at the ordinary temperature, after which the temperature is raised gradually, commencing at 25°, increasing to 28° during the next 3 days and then slowly to 32°–35° at which it is kept until dry, usually 8 to 14 days. Starch dried at too high a temperature during the earlier stages, loses its colour and brightness and may become quite yellow.

Fermentation should be prevented as much as possible, as it prevents the deposition of starch in the settling tanks by reason of the evolution of gas and the presence of gas when drying cause them to break irregularly. Sulphurous acid or some other like agent is usually employed to prevent fermentation.

The dried starch contains about 12 p.c. of water, but on exposure to air it absorbs moisture up to 15 p.c., which is the commercially recognised standard. If it be desired to obtain the starch in large lumps, the blocks, after scraping, are cut up into smaller pieces, which are then slowly dried in the air.

Waste products. These consist of gluten and impure starch. They may be mixed, and used for cattle-feeding; or, more or less separated and utilised, the starch for feeding, and the gluten for manurial, purposes.

21. *Manufacture of starch from maize.* This process is principally confined to the United States, and no industry in that country has grown so rapidly and concentrated itself into a small circle of factories within the last half century as the manufacture of starch from maize or Indian corn, which is there termed corn-starch. An interesting account of this industry is given by Dr. G. Archbold, in J. Soc. Chem. Ind. 1887, 80–84 and 1902, 4–9, of which the following is an abstract:—

The average composition of maize or Indian corn used in American factories is as follows, and is known as No. 4.

	p.c.
Oil	5·20
Carbohydrates (starch therein 54·8 p.c.)	71·22
Proteids	10·46
Ash	1·52
Water	11·60
	100·00

Process of manufacture. Many improvements have been introduced in late years, and all the older processes, with one exception, are no longer used. This exception, known as the 'Chemico-Mechanical' process, is a secret process, producing a starch which no other process appears to approach in purity. Advantage is taken of the fact that maize or Indian corn contains two albuminoids which envelop the starch, one of these is soluble in water and the other in weak caustic alkali solutions. The process consists primarily of extraction of these bodies from the corn so that the resulting starch, as it passes through the various cleansing and drying processes, is absolutely free from everything likely to set up fermentation and acidification, whereby the final product would be injuriously affected.

The process in most general use in the United States is that known as the sulphur dioxide process or that process combined with alkali in the later stages. The sulphur dioxide process throughout is used by glucose makers with advantage.

There is a later process, known as the attrition or dry process, which promises a new era in the starch industry, should it ever be brought to perfection, which it is very far from at present. It consists in grinding the maize in an attrition mill and separating the constituents by means of a blower, the starch then being purified as in other processes.

In the extraction of starch from maize by the sulphur dioxide process, the dry grain is conveyed from the granaries to large hopper-bottomed steeping vats, made of 2-inch pine about 14 ft. deep and 12 ft. diameter. Water, impregnated with about 1 p.c. of sulphur dioxide, is run in upon it and is kept in circulation by means of steam syphons and at the same time heated and maintained at temperatures varying from 120° to 140°F. Steeping is continued for 2 to 4 days, according as the corn is amenable to the softening and disintegrating process to follow.

The following figures show what takes place during steeping:

	lbs.
Original bushel of corn weighed .	56·0
Water contained in this . . .	6·5
Weight of steeped corn, subsequently dried at 100° *in vacuo* . . .	49·44

This shows a loss due to the washing away of oil, albumenoid and ash of 0·06 lb. or 1 oz. per bushel of corn. The water absorbed by each bushel of corn is 29·75 lbs. or about 3 gallons.

The steep waters may be run to waste or evaporated for the recovery of the soluble material therein for the manufacture of cattle food. In this wet and softened condition the grain is conveyed to the crushing room, where it is run through Foos mills or their equivalent, by which means it is cracked, decorticated and partially ground, giving rise to a diffluent mass. This is diluted with water so that the most finely ground portions form a liquor (separator liquor) and is passed through the Degerminator —a large long V-shaped tank fitted with a screw conveyor in the bottom and skimming paddles at the top. The oil-bearing germ floats and is skimmed off while the endosperm, starchy and glutinous matter, cortical tissues, bran and fibrous matter pass on. The oil bearing germ is conveyed away, washed free from adherent starch, dried, ground, 'cooked' with live steam, and its oil expressed in hydraulic presses. The resulting products are:

Corn oil, used in manufacture of soap;

Oil cake or *maize germ cake*, used as cattle food.

The cortical and endospermal portions, the most finely ground of which are termed separator liquor, are screened by passing them over a vibrating copper sieve. The coarse material separated is caught in an elevator and conveyed to the grinding room where it is ground with the necessary quantity of water in two or three burr stone mills built for grinding wet corn, and then pumped to feed vats fitted with stirring gear and combined with the previously separated 'separator liquor.'

This mixture is delivered from these tanks on to a series of shakers. These are wooden frames about 9 ft. by 4 ft., fitted with No. 10 bolting cloth of the best material in three or four sections which receive a vibratory motion by means of an eccentric shaft, the shakers themselves being set upon hickory sprains to give a soft but rapid motion. When run through these shakers the milky fluid has sp.gr. of 3°Bé on an average, and contains in one gallon about 5·42 oz. of pure starch and 1½ oz. of dry feed.

The separated unground portion is conducted back to the mills for a second grinding and then goes a second time over the shakers.

The branny portions of the grain or 'wet feed' left on the shakers is conveyed to a stirring tank mixed with water, passed over a second series of shakers, where it is washed as free from starch as possible, and conveyed to presses where it is practically freed from water, and emanates therefrom as 'press feed,' or is dried in an appropriate apparatus and sold as corn bran. Its composition is as follows:

Moisture	8·93
Proteids	10·50
Fat	2·75
Carbohydrates	65·04
Fibre (insoluble) . . .	12·30
Ash	0·48
	100·00

The liquors from the shakers and mill, now known as 'mill liquor' or 'crude starch liquor,' are sometimes passed over another series of sieves or shakers to remove the more or less gritty, glutinous and fibrous residues, or they flow immediately over runs, trays, tables or gutters as they are variously termed. These runs are made of wood and are in 16 sections, 120 ft. long and 6 to 8 in. deep. Each section is divided into 3 canals, 18 in. wide, by means of partitions, and is inclined at an inclination of ⅜ in. in every 12 ft.

The starch liquor is allowed to flow on each division of the tables at the rate of 1 gall. per 35 secs. at a density of 3½°Bé. Here the suspended impure starch is deposited almost completely, the liquor containing the glutinous and other residues flowing off at the ends at the rate of 1 gall. per 20 secs., having a sp.gr. of ½°Bé., the deposition of starch having caused the lowering of the density to this degree.

These run tailings are conducted into continuous settling tanks, where the solids are allowed to subside while the clear supernatant liquid is syphoned off and run into sieves. The so concentrated liquor is sold as a liquid feed under the name of 'slop' or 'swill,' or may be passed through filter presses and the solid material sold as gluten meal. The 'green starch,' which has been deposited on the runs, containing about 50 p.c. of moisture, is shovelled off and stirred up with water in the 'breakers.' These are wooden vats several feet high, the diameter of which is equal to the height, and are provided with agitators. The starch is here mixed with water to produce a mixture having a density of 7°Bé, and according to the use for which it is destined may or may not receive at this stage a chemical or alkali treatment with caustic soda before going on to the runs a second time.

If it is to receive alkali treatment the agitators are set in motion and a solution of caustic soda at 3°Bé very cautiously added until the milky liquid has changed to a greenish-yellow colour. The action of the alkali neutralises any acidity and precipitates a small proportion of the dissolved albuminoids, and the excess of alkali dissolves or emulsifies the oil, dissolves the gluten and coagulates and discolours the mechanically divided fine feed and insoluble gluten (that which acids alone dissolve). From the breakers or alkali tanks, it is pumped to the regulators, usually four wooden vats fitted with agitators, where it is reduced to 3° or 3½°Bé., and thence flows over the table or runs once more.

The deposited starch is transferred once more to the breakers, where it is mixed with water and run direct to the boxes, or first reduced to a gravity of 11° to 12°Bé and allowed to run on to a second series of shakers, where it is separated from fine coagulated matter, and passes through at about 8°Bé. This liquid is then run into settling vats, 10 ft. diameter by 10 ft. deep, in which at various heights up the sides are openings fitted with valves. The starch is allowed to settle in these vats and the impure water is run through the valves in the sides. Fresh water is now added and the liquor made up to a gravity of 23° to 24°Bé. The thickened purified starch liquor from the 'breakers' or settling vats now runs into a series of boxes, made of pine 7 in. × 7 in. × 5 ft. 7½ in. long, the sides being slightly inclined and having a perforated bottom to admit of drainage. These boxes are placed on a table and allowed to drain overnight when the moisture content is reduced to 55 p.c. It is then dumped from the boxes and the oblong blocks cut in pieces of about 12½ lbs. weight, placed on an absorbent medium or floor, generally made of porous brick covered with a layer of plaster of Paris cement, and heated underneath by means of a series of steam pipes. Here the starch remains for some hours until the moisture it contains is reduced to about 45 p.c. It is then ready for the crushing process. The blocks of starch are placed side by side on a rack or shelves in a kiln, and allowed to remain therein exposed to a heat of 120°–130°F. until a yellowish-brown crust forms on the outside, varying in thickness from ⅛ to ¼ in. They are then taken out and the crust removed, when the interior appears perfectly white. In this state it is wrapped in paper, and again returned to the kiln, and now exposed to a temperature of 156°–176°F. for a period varying from 3 to 15 days or sometimes even longer. During this time the blocks of starch separate up into a series of irregularly shaped rods resembling prisms, more or less, and are technically termed 'crystals.' A high temperature and short period in contact therewith gives small pipe 'crystals,' whilst with a low temperature and longer time the starch is obtained in larger chunks and more irregular.

The browned starch which has been removed from the blocks is returned to the washers, alkali added and again run over the tables and shakers, boxed, tiled and dried as with the former starch.

The methods of drying have been considerably improved within recent years, whereby the time taken is considerably reduced and the quality of the starch improved.

The purified starch liquor is run into specially constructed boxes lined with muslin and arranged on a table provided with a vacuum chamber, the moisture being extracted from the starch by means of a vacuum pump. By this method the crushing and scraping processes become unnecessary. The starch from the boxes is cut into 7-in. cubes and placed in drying kilns arranged with a current of hot air and an exhaust for moist air, the time for drying being reduced by this means from weeks or days to hours.

There are two types of starch on the market known respectively as (1) 'thick boiling' starches either 'chemicalled,' *i.e.* prepared by treatment with alkali, or 'unchemicalled,' in which no alkali has been used, the starch instead being put over the runs a second time and dried more or less slowly. These unchemicalled starches are used for baking powder or as a size in textile industries; (2) 'thin boiling' starches prepared by two processes termed the drying-in process and the in-suspension process.

In the 'drying-in process,' unchemicalled starch is suspended in water to about 22°Bé, and a certain quantity of hydrochloric acid added to the mills. It is then boxed and drained and the starch containing 42–43 p.c. of moisture is broken up and dried. During this process, the small quantity of hydrochloric acid converts some of the starch into the soluble form, the starch thereby producing a paste with considerably less viscosity.

In the 'in-suspension' process the starch, suspended in water at about 22°Bé, is heated at a temperature well below the gelatinising point with a small quantity of sulphuric or hydrochloric acid, the liquid being constantly stirred. It is then boxed and dried in the usual way.

These thin boiling starches, used principally in the laundry and confectionery trades, produce a paste on boiling with water of much less viscosity than the ordinary or thick boiling product, the degree of viscosity being regulated according to their application. Starches prepared from maize in this way are capable of yielding as good results in the laundry as starches from rice or wheat or any blend of such starches.

22. *Manufacture of starches for edible purposes.* Alimentary substances may naturally be divided into three well-marked groups—carbohydrates, proteids, and fats; and of these fully two-thirds, or perhaps more, of the food of mankind belongs to the carbohydrate group, of which starch is by far the most important member.

In the raw state, according to Roberts (Digestive Ferments, p. 17), starch is to man an almost indigestible substance, but when previously subjected to the operation of cooking it is digested with great facility. Diastase has, at best, only a comparatively feeble action on the unbroken starch granule, even at the temperature of the body. By the aid of heat and moisture in the process of cooking the starch granule is much more effectively broken up, and in the gelatinised state is very rapidly attacked and digested by the diastatic juices of the body.

In addition to the large quantities of starch consumed in the natural form—as rice, potatos, bread, &c.—numerous forms of prepared starches are met with in commerce as articles of food. These differ in a most essential degree from wheat and other cereal flours in that they consist almost entirely of absolutely pure starch granules, which very readily gelatinise and become easily assimilated.

In this country large quantities of edible starch are manufactured from maize and rice, whilst in France potatos are largely employed for the same purpose. The colonies furnish a very large proportion of edible starches, the principal being arrowroot from the West Indies, Natal, India, Fiji, and Queensland.

23. *Cornflour.* Although the manufacture of starch from maize has been practised in this country for the last fifty years, the product therefrom—known under various names, such as Indian cornflour, oswego, maizena—has been used chiefly for edible purposes, whilst most of the starch used for other household as well as manufacturing purposes has been that made from wheat and rice.

This industry is centred in Paisley, Scotland, having been first introduced by Polson (Eng. Pat. 1854, 1068). The process of manufacture is now, however, practically identical with that employed in America, the raw material being maize or Indian corn imported from various, and often widely different sources.

Large quantities of rice starch are treated in a somewhat similar way, and sent out for dietetic purposes, under the name of British cornflour and other fancy names.

24. *Arrowroot starch* or arrowroot is derived from plants of the genus *Maranta*, the most important member of which is *Maranta arundinacea* (Linn.), a native of the West Indies, and which furnishes most of the genuine West Indian arrowroot. Three other species of *Maranta* are also cultivated for the production of starch: *M. nobilis*, *M. Allouia* (Aubl.), which grow in the West Indies, and *M. ramosissima* (Wall.), which is a native of the East Indies.

The arrowroot plant is herbaceous, from 4 to 6 ft. high, and has broad, pointed leaves. The tuberous roots or rhizomes are pointed, covered with scales, and sometimes a foot in length and about the thickness of a finger.

The starch is stored in the rhizomes of the plant, and requires to be extracted and purified to render it fit for market.

The following details of manufacture are taken from a paper by J. W. Macdonald, on 'The Manufacture of Arrowroot Starch in St. Vincent' (J. Soc. Chem. Ind. 6, 334).

The first part of the manufacturing process is to soak the roots in water, to soften the covering and the adhering earth. They are then stripped of the covering and washed, and thrown into a second or rinsing tank. When thoroughly clean they are taken to the pulping machine. The skin is said to contain a resinous matter, which gives a yellow tinge and unpleasant flavour to the starch if the latter is not well washed. In former times the roots were skinned with German-silver knives before being pulped. This is said to have produced whiter starch; but as it was so laborious and expensive, it was discontinued. The skinned roots were pulped by subjecting them to great pressure by passing them through an upper, and then a lower and much closer, pair of brass rollers, to break the starch cells. The method of pulping now generally adopted is to feed the clean unskinned roots against a fine saw grater very similar to a potato grater. It is a solid cylinder of hard wood, about 23 in. diameter and 7 in. wide. Slits are made by a saw from end to end of the wood at half-inch intervals. Saw blades having 6 to 10 teeth to the inch are then fitted into the slits, and the whole immersed in water to swell the wood and fix the saws. The grater is now fitted into its place very close to a wooden feeding bed. As it revolves several hundred times per minute, it tears the roots into shreds. A great deal, however, depends on the fineness of the teeth and the velocity of the drum.

On account of the very fibrous nature of the pulp, there is considerable difficulty in the sieving or separating of the starch from it. The fibres readily gather into lumps and inclose the starch, so that hand-sieving, although very tedious, has to be resorted to. The pulp is first run into a box or sieve, the bottom of which is a sheet of copper or tin punched with holes one-fifth of an inch diameter. While water flows on, the contents are kept thoroughly agitated by hand until all the starch has been washed out. While one strainerful is being washed, another is being filled, so that there should be no delay. However careful one is, there is a loss of starch in the fibre, owing to the presence of small bits of roots which have escaped pulping.

In one factory a stationary half-cylinder is employed. Its under side is pierced with small holes; but there is a slide under this to open or close at will. Inside there are rakes attached to two shafts, which move in opposite directions and cause the rakes to oscillate very rapidly between each other, thereby keeping the fibre always open. The starch water is let out, more water run in, and the operation repeated until all the starch is extracted, after which the fibre is taken out. The great objection to any mechanical washer is the tendency of the fibre to accumulate on the agitators and break them. To get over this difficulty it has been proposed to chop up or slice the roots into small, short pieces, and either rasp them or pass them through metal rollers or millstones, so that the thin disintegrated pulp may flow over mechanical sieves. Although causing a loss of starch, the present method of rasping avoids an undue pulverising of the soft yellow fibre, and so gives a very white starch without much trouble.

From the fibre-strainers the starch water flows consecutively through a series of brass wire sieves of 40, 80, and 100 meshes to the inch; each of these retain small fleshy bits of unpulped root. From the last sieve the water runs into the settling cisterns, which are preferably lined with white glazed tiles to avoid accumulation of slime.

A portion of fibre collected on the finer sieves is used for feeding the animals on the estate; the remainder, and all the coarse fibre, is used as manure. For this purpose it is left in heaps until it decomposes, after which it is distributed on the fields along with pen manure; sometimes ashes and guano are used. The waste water from washing the starch contains a considerable amount of vegetable matter, and gives good results where it is run on the fields; but the extensive application is not practicable. After the starch has settled in the cisterns the water is run off, and more added; the whole is stirred up again, and allowed to settle. This generally suffices to dissolve out soluble matters. At night all the cisterns are drained, and the starch is dug out and taken to a mixing-box, where it is mixed with a small amount of water, then run through another fine sieve into the separating pans. These are small round galvanised cisterns, with smooth perpendicular sides. When filled, the starch-milk is stirred round with a small oar until it is in violent circulation. The oar is withdrawn, and the cisterns left until morning. The stirring has the effect of separating the starch from any remaining impurities. These, being of less specific gravity, settle last, and therefore on the top of the starch. Next morning the water is drained off, and the light, impure starch scraped off the surface. If the earlier parts of the process are carelessly done, this separation may have to be repeated before the starch is quite pure. The impure surface starch contains a large proportion of starch entangled in very fine particles of fibre and broken cell walls. Although this can be dried and exported as an inferior starch, it is generally given to the labourers as a perquisite. It is used in various forms as flour. Poultry and pigs are also fed with it. Weak caustic soda extracts a colouring matter from it, but also precipitates a yellow substance, making it very difficult to separate the starch from it in a pure state.

The pure starch in the separators is now taken out in blocks, and placed on trays for about 12 hours to dry and harden. It is then broken into smaller pieces and taken to the drying house, where it is air-dried, the building being open on all sides for free circulation. It is surrounded, however, with galvanised wire to keep out the small birds which hover about. Inside there is a series of wire shelves over large shallow wooden trays. The top shelf is made of very open wire, the next is closer, and so on, the lowest being the closest. The wet lumps of starch are placed side by side on the top shelf, where they remain until, by the action of the air, they crack up and fall through to the next shelf. In time the whole falls through the lowest shelf, and is in a fine granular state, ready for packing. It contains from 14 to 17 p.c. of water. In cold, wet weather the starch dries very slowly, taking sometimes as long as two weeks. During this time, if it has been imperfectly purified, the lumps get sour and become yellowish. Indeed, the whole process must be as rapid as possible. In the settling cisterns especially, if the starch is left in contact with the impure water too long, its whiteness is affected. The crop lasts from October to May. The name ‘arrowroot’ is probably derived from the Indian word Ara-ruta, or ‘mealy root’; but some say that this root has been confounded with the *Maranta Galanga* (Linn.), which was called the arrowroot on account of its bruised roots being employed as an antidote to the poison of the *Manihot utilissima* (Pohl), used for poisoning arrows.

Regarding the yield of arrowroot, an acre will produce 13,000 to 15,000 lbs. of roots, according to the season; in wet seasons the roots are heavy and moist, and give less starch. A fair average yield is 22 cwts. air-dried starch, with 14 p.c. water, per acre, or about 19 p.c. on good roots. There is no doubt this can be considerably increased by the use of improved pulping and sieving machinery.

The following analyses will give an idea of the constituents of the roots, as well as of the composition of the finished starch:—

	Roots	Starch
Starch	27·07	83·70
Fibre	2·82	0·04
Fat	0·26	0·07
Albumen	1·56	—
Sugar, gum, &c.	4·10	0·18
Ash	1·23	0·14
Water	62·96	15·87
	100·00	100·00

The ash consisted of calcium phosphate and alkaline sulphates and chlorides.

Arrowroot starch swells much more readily and with less heat than maize, rice, or wheat starch, and forms a stiffer jelly. It is, therefore, well adapted for sizing and laundry purposes. As an article of food it must be regarded as the purest, most digestible, and palatable of the starches.

Methods similar to the above are employed for the extraction of arrowroot starch in the East Indies, Natal, and Queensland.

25. *Cassava starch* or *Brazilian arrowroot*. The root which produces this starch is somewhat similar to that of the *Maranta*, and is known as Cassava or Manioc. It belongs to the genus *Manihot*, the most important of which is *Manihot utilissima* or *Jatropha Manihot*, a native of Brazil, but now cultivated in India, Guiana, West Indies, and various parts of Africa. In Brazil considerable attention has been given to the manufacture of starch from various tubers and roots; but cassava starch is

the principal kind which is manufactured there, and is known as Brazilian arrowroot. Its mode of preparation is very similar to that of East Indian arrowroot.

Tapioca is prepared by heating the cassava starch whilst still moist upon hot plates, keeping it well stirred with an iron rod all the time. A large number of the starch granules burst during the process of heating, and adhere together in small irregular masses, in which form it is imported into this country. Tapioca is partially soluble in cold water, and readily swells up in boiling water, forming a transparent jelly.

The natives of Brazil prepare cassava meal by reducing the tuberous roots to a pulp either by rasping or grinding, after having first washed and peeled them. This pulp is then placed in bags made of plaited reeds, and subjected to pressure, so as to express the juice. The residue —consisting of a mixture of starch, vegetable fibre, and albuminous matter—is partially dried in the sun and partially on hot plates over a slow fire, and kept continually stirred with a wooden spoon until it is dry, but not browned; it is then known as cassava meal, and used for making bread. The juice is allowed to stand for some time, when the starch contained in it subsides, and is washed with water, constituting a finer meal. The roots of the species known as bitter cassava contain an acrid poison, hydrocyanic acid, which, being volatile, is readily dissipated by heat, or may be washed away with water.

26. *Curcuma starch.* In the East Indies a starch is prepared from the tuberous root of *Curcuma angustifolia* (Roxb.), which is sometimes known as East India arrowroot, and said to be rather extensively manufactured in Travancore and other parts of North-west India.

27. *Arum starch.* A starch very much resembling cassava starch, and which was used as a substitute for arrowroot, and known in the market as Portland arrowroot, was obtained from the roots of the wild arum, or *Arum maculatum* (Linn.), this plant being formerly cultivated in the Island of Portland for this purpose.

28. *Tous-les-mois.* This starch, the granules of which are the largest known, is extracted from the rhizomes of the *Canna edulis* (Ker-Gawl), a native of the West Indies, principally at St. Kitts. That which is imported into this country is used partly in the manufacture of cocoa and partly in the preparation of food for infants.

29. *Sago.* This is the name given in commerce to a prepared starch obtained from the pith of several varieties of palms, which are indigenous to the Malayan archipelago, the Philippine Islands, and parts of India, wherever there is a soil suitable for their cultivation. This consists of marsh or bog land, composed of decayed vegetables, near the sea. The principal species are the following: *Metroxylon Sagus* (Roxb.), *Raphia pedunculata* (Beauv.), *Borassus flabellifer* (Linn.), and *Arenga saccharifera* (Labill.).

All these palms propagate themselves by lateral shoots as well as by seed, so that a sago plantation, when once formed, may be said to be perpetual. The growth is slow at first, but when once fairly started proceeds rapidly, until a height of some 20 to 30 feet is attained by the stem.

The sago tree, when cut down and the top severed from it, represents a cylinder about 20 in. in diameter, and from 15 to 20 ft. in length, consisting essentially of a hard woody tube, the interior of which is filled with starch granules intermixed with fibrous matter. From such a tree about 700 lbs. of starch would be extracted, so that three such trees would yield nearly double as much food material as one acre of wheat. Sago is, however, far from being either so palatable or nutritious as it is prolific, and even where it is more abundant is never preferred to rice.

By far the greater portion of sago imported into this country comes in the raw state as sago flour, and is used to a very large extent in the manufacture of glucose. Singapore is the headquarters for exportation of sago, both raw and manufactured being brought there from the islands to the eastward, principally from the north-west coast of Borneo and the north-east of Sumatra, with its adjacent isles from Siak to Indragari, as well as from many other places more distant.

To obtain the starch or flour, the trees, as soon as they have arrived at a suitable stage of growth, are cut down close to the roots, the stems sawn into pieces 7 or 8 ft. long, which are split open and the pith extracted. This is then pounded up in wooden mortars so as to reduce it to powder, agitated with water in a trough, run through sieves to free the starch from cellular tissue and fibrous matter, allowed to settle, and, after washing several times with water, is dried and sold as sago flour.

What is known as granulated or pearl sago is prepared from sago flour in the following manner:—The flour is made into a stiff paste with water, and rubbed through a metal sieve into a heated, very shallow, copper or iron pan, greased inside with vegetable fat. During the process of heating, the starch granules are kept constantly agitated, a portion of them swelling and becoming pasty serve to bind the remainder of the granules together. The resulting cohering particles obtained in this way are called pearl sago, of which two kinds are known in commerce, one consisting of small grains about the size of rape seed, and the other of grains about two or three times the size.

Granulated sago appears to have been introduced into Europe in the early part of the eighteenth century, but there is reason to believe that the starch from the sago palm has been used as an article of food by the natives of those countries in which it grows from a very remote period.

A sample of pearl sago gave on analysis:

Starch	84·64
Water	15·22
Mineral matter	0·14
Total	100·00

In later times, in Germany and France, sago has been made from potato starch, and introduced into commerce as 'Indian sago,' the best specimens of these imitations surpassing real sago in appearance and whiteness; so that the question arises, Is there any essential difference between the European imitation and the real sago of the tropics? Opinions as to goodness of flavour differ, and in reference to the nutritive values of the two there have been no scientific investigations. *A priori*, it is not impossible that the nutrient value of the real is greater than that of the artificial, since the former contains more granulose. However, the difference between the relative values of the two is not nearly so great as the difference in price, which stands almost as 1 : 2.

Sago has the property of swelling up in hot fluids without losing its coherence; the granules do not fall to pieces, but appear as transparent and gelatinous, but not sticky, spheroids.

30. *Inulin.* In the tubers of the dahlia, Jerusalem artichoke, and other plants of a similar character, there occurs an amylaceous substance which bears a very close resemblance to starch, having identically the same ultimate composition, and which, indeed, for all practical purposes may be regarded as another form of starch. To this substance the name of *inulin* has been given. It is a white hygroscopic powder or sphaero crystals, insoluble in absolute alcohol and sparingly soluble in dilute alcohol. It has the power of reducing ammoniacal silver nitrate.

Kiliani (Annalen, 205, 145) prepares inulin as follows. Roots of *Dahlia variabilis* (Desf.) are well washed, and, after being rasped, are boiled with water in the presence of sodium carbonate. The liquid obtained is cooled by means of a freezing mixture, allowed to stand some time, and the precipitate which settles out dissolved in hot water, filtered while hot, and again exposed to a freezing mixture. This process is repeated three or four times, after which the inulin is obtained as a perfectly white substance. It is then treated with alcohol, whereby any lævulose that may be present is removed, and the inulin finally dried over sulphuric acid *in vacuo*.

Inulin is not acted upon by diastase, but is converted into lævulose when heated with dilute acids.

31. *Lichen starch.* In Iceland moss there occurs a form of starch easily soluble in water, from which it is thrown down as a flocculent precipitate by alcohol, and which gives the characteristic blue colouration with iodine. It rotates polarised light strongly to the right, and is readily converted by diastase into dextrin and maltose. Lichen starch, therefore, appears to be a soluble, unorganised modification of ordinary starch.

32. *Glycogen.* In the livers of most animals there is produced a white amorphous substance which forms an opalescent solution with water, from which it is precipitated by alcohol, and is transformed into dextrin and maltose by the action of diastase, and to which the name of glycogen has been given. It has a formula $C_6H_{10}O_5$, specific rotatory power $[\alpha]_D + 197°$, and gives a wine-red colouration with iodine. It may be regarded in every sense as an exact counterpart of soluble starch, and is considered to be reserve starch material elaborated from the sugars and other carbohydrates consumed as food.

33. *Detection of starch.* The presence of starch existing in the solid state in any substance is most readily detected by microscopic examination, supplemented, where necessary, by the addition of iodine solution to the slide, when the characteristic blue colouration is at once observed if any starch granules are present. In this way the presence of starch in chlorophyll granules may be readily detected by Sachs' method (Chem. Zentr. 1884, 945). The fresh green leaves are plunged into boiling water for 10 minutes; certain soluble substances are thereby extracted, whilst the starch and colouring matter of the chlorophyll grains remain intact. A short immersion in 96 p.c. alcohol now removes the green colouring matter and certain bodies soluble in alcohol, leaving the starch behind in the colourless tissue, the decoloration proceeding more rapidly in sunlight or warm alcohol than in the dark and cold. After this treatment the leaves are placed in a strong solution of iodine, made by dissolving iodine in alcohol, and then diluting with distilled water until the liquid has a dark-brown colour. They are allowed to remain in this liquid for about an hour, or until they no longer acquire colour. If no starch is present the leaves are simply stained yellow; if they are stained slightly black, very little starch is present. If a large quantity of starch exists in the cells, the tissue appears blue-black or black, with a metallic lustre, the venation appearing as a pale network in the dark ground. By this means the absence of starch from etiolated leaves, from the white portions of variegated foliage, and from those portions of the leaf which have been covered by paper or tinfoil, may be readily demonstrated.

When a sample of a substance supposed to contain starch is to be examined under the microscope, it is first reduced to a fine powder, if not already in that state; a small quantity of it is then mixed with some water in a watch-glass by means of a glass rod, and a drop of the mixture placed on the slide, a cover glass put on, any superfluous moisture round the edges of the cover-glass carefully removed with blotting-paper, and the slide next placed under the microscope; the stage should be illuminated with rather oblique light, a ½ or ¼ inch objective, with a B eye-piece, being the most suitable magnifying power to employ.

The following points should be observed: the size and form of the granules, the position and character of the hilum, the nature of the striæ or concentric rings, and the appearance presented by the granules under polarised light. In the latter case, it is advisable to mount the sample in glycerin instead of in water; a red-green selenite plate may also be advantageously employed. It is only by careful microscopical examination that one particular form of starch can be differentiated from another, and it is comparatively easy when only one kind of starch is present; but when mixtures of different starches occur in the same sample, the detection of each particular one becomes a matter of some difficulty.

The following method, as given by Bell (Chemistry of Foods, 2, 151), appears to be practicable for most of the commonly occurring varieties:—

To insure the homogeneousness of the

sample, it is first rubbed in a mortar, and passed several times through a sieve. A small quantity, say 0·5 of a grain, is then weighed out and placed upon a glass slide, where it is worked into a thin paste with about two drops of water. A thin covering-glass, measuring about 1½ inch by 1 inch, is then placed over the paste, and moved about the slide until the paste is equally distributed and all under the covering-glass. With a ¼-inch objective and B-eyepiece the number of granules of foreign starch is counted in nine 'fields,' as fairly as possible representing the entire slide. The process is repeated until a correct idea of the composition of the sample is obtained.

Standard mixtures approximately representing the sample are then made up and treated in exactly the same way, and, from a comparison of the results, the percentage of foreign starch is computed.

When the percentage of foreign starch is large it is advantageous, in order to facilitate the counting of the granules, to insert in the eye-piece a slide accurately divided into squares.

In cases where the granules of added starch are so small and numerous that it is impossible to count them, as with rice starch, a similar process of preparing the slides is followed, and as correct an estimate of the foreign starch is made as is possible by a comparison of the appearance of the sample with that of the standard mixtures.

It is often advisable to use a dilute solution of iodine instead of water in preparing the slides for examination, as the resulting colouration of the starch granules renders them more distinctly visible.

Sometimes it is desirable to remove the colouring matter from the solid substance, and if cold water fails to effect this, alcohol and other solvents should be tried. Successive treatments of the substance with cold water and alcohol, however, will usually render the starch observable microscopically without having recourse to other solvents.

As an aid to their microscopical examination and recognition, Allen (Commercial Organic Analysis, 335; revised edition 1909, 411), following Muter, arranges the starches into five classes, having the following general characteristics :—

I. **The Potato Group** includes such oval or ovate starches as give a play of colour when examined by polarised light and selenite plate, and having the hilum and concentric rings clearly visible.

II. **The Leguminous Starches** comprise such round or oval starches as give little or no colour with polarised light, have concentric rings all but invisible, although becoming apparent, in many cases, on treating the starch with chromic acid, while the hilum is well marked, and cracked or stellate.[1]

III. **The Wheat Group** comprises those round or oval starches having both hilum and concentric rings invisible in the majority of granules. It includes starches from wheat and some other cereals, and a variety of starches from medicinal plants, such as jalap, rhubarb, senega, &c.[1]

IV. **The Sago Group** comprises those starches of which all the granules are truncated at one end. It includes some starches used for food, together with those from belladonna, colchicum, scammony, podophyllum, canella, aconite, cassia, and cinnamon.

V. **The Rice Group** contains the starches, all the granules of which are polygonal in form. It includes the starches from oats, buckwheat, rice, pepper, and ipecacuanha.

34. *Microscopical appearance of different varieties of starch.* The microscopical appearance of the different varieties of starch granules is shown in the following illustrations, which are taken from Dr. Bell's Chemistry of Foods, Pt. II.

Class I.—(*a*) *Canna*, or *Tous les mois* (Fig. 15). The granules of this starch are the largest known, are ovate in form, rounded at one end, and more or less pointed at the other, near which is situated the circular hilum. The rings are well marked, but not complete.

(*b*) *Potato* (Fig. 16). Granules vary much in form, the smaller ones being more or less spherical, whilst the larger are ovate or oyster-shaped. The hilum, which may be circular or stellate, is generally near the smaller end. In the larger granules the concentric rings are very distinct and complete.

(*c*) *Maranta* or *arrowroot*. According to Bell, *Bermuda arrowroot* (Fig. 17) may be taken as the most perfect type of a maranta starch. In no other kind of arrowroot do the granules so generally exhibit an irregularly oval form, with the peculiar, small, nipple-like projection near one end, where also is situated the hilum, which is either circular or linear. The rings are concentric and numerous, always visible, but not strongly marked.

(*d*) *Natal arrowroot* (Fig. 18), as compared with Bermuda, may be taken as an example of the divergence which occurs in the form, size, and general appearance of the starch granules yielded by different varieties of maranta. The hilum is generally linear. The rings are very distinct under water.

Class II.—*Bean*, *Pea*, and *Lentil* (Figs. 19, 20). These starches are very similar in appearance, and not distinguishable from one another in mixtures. The granules are oblong, kidney-shaped, and irregularly formed, most of them having a longitudinal cavity running along each granule lengthwise, and from which, in many instances, furrows diverge to the right and left, imparting to their surfaces a fractured appearance.

Class III.—*Wheat* (Fig. 21). The granules, which are nearly circular, present a flattened appearance under the microscope, and are generally of two sizes—large and small. Hilum central; rings concentric and very faintly marked.

Barley (Fig. 22). The granules are very similar to those of wheat, but rather more irregular in shape.

Rye (Fig. 23). The granules of this starch

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[1] All these starches present very close resemblances, and are generally indistinguishable from each other when in admixture.

[1] The cereal starches may be divided into two well-defined groups, wheat, barley, and rye starches being circular, or nearly so, while the starches of rice, maize, buckwheat, and oat are polygonal.

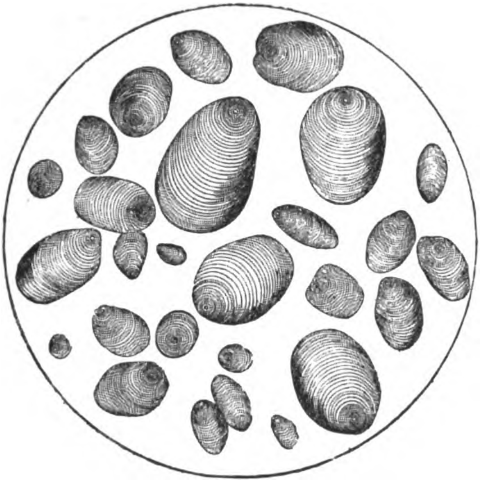

Fig. 15.

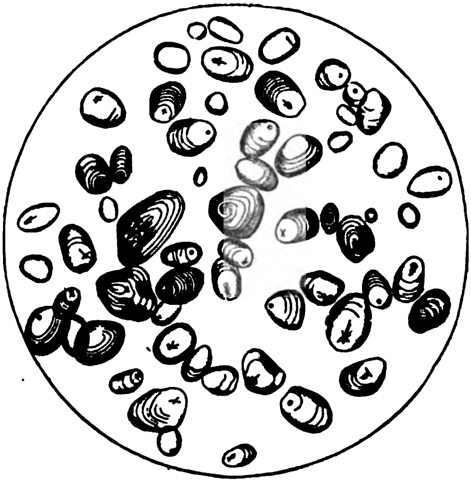

Fig. 16.

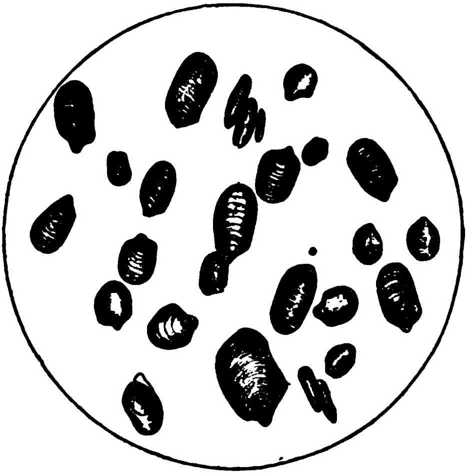

Fig. 17.

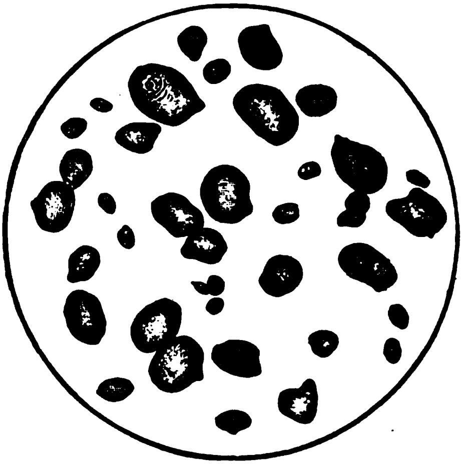

Fig. 18.

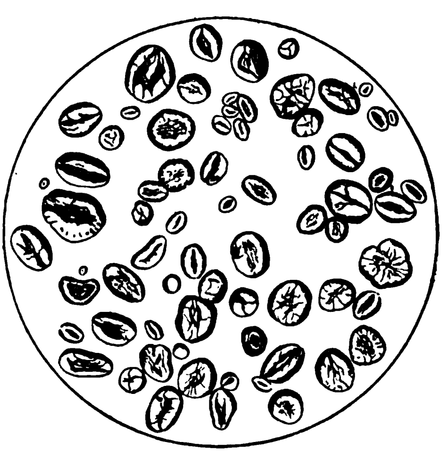

Fig. 19.

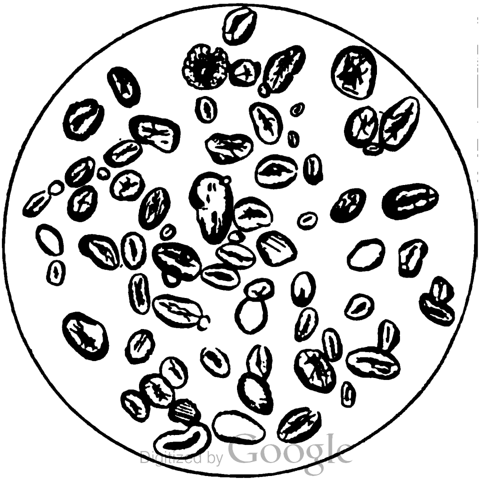

Fig. 20.

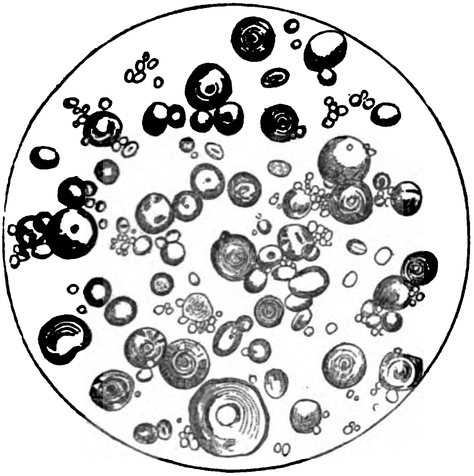

Fig. 21.

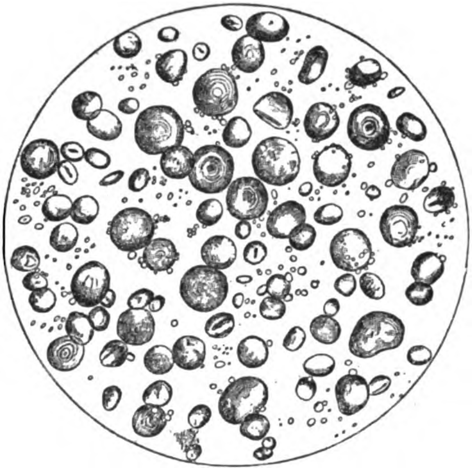

Fig. 22.

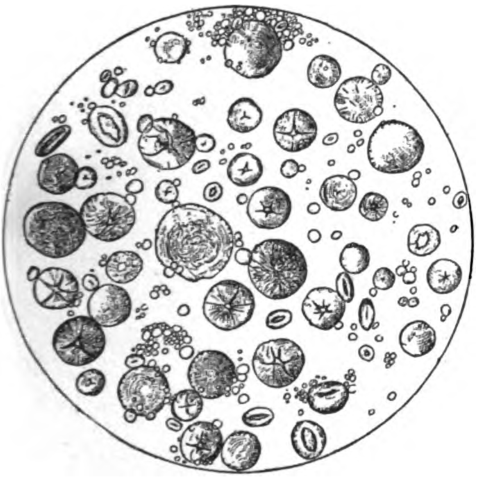

Fig. 23.

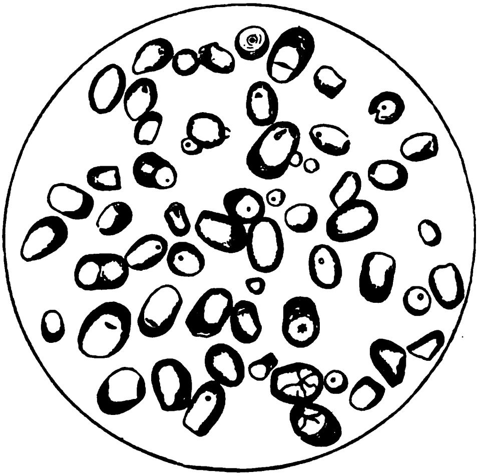

Fig. 24.

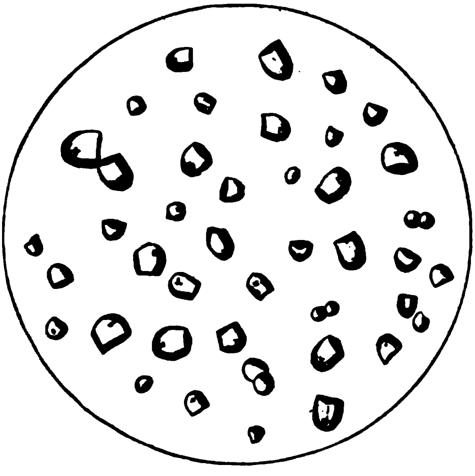

Fig. 25

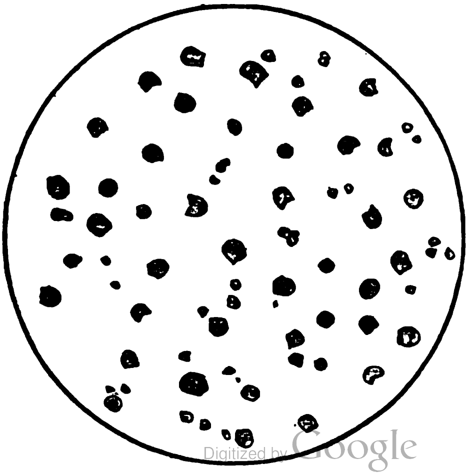

Fig. 26

are larger than those of wheat or barley, are more circular in form, and present a flattened appearance and fractured surface. The hilum in the majority of the granules is stellate.

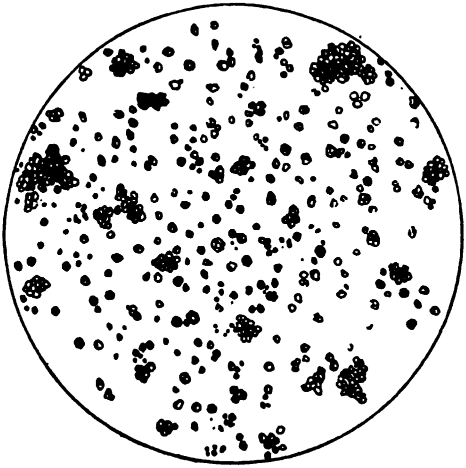

Fig. 27.

Class IV.—*Sago* (Fig. 24). The granules are elongated, rounded at one end and truncated at the other. Hilum circular, stellate, or linear, near convex end. The rings are concentric, numerous, and but faintly visible.

Cassava (Fig. 25). The granules are similar to those of sago, but not so elongated, presenting more the appearance of a kettledrum. The hilum, which is well defined, is situated near the centre.

Arum (Fig. 26). Somewhat like cassava, but much smaller.

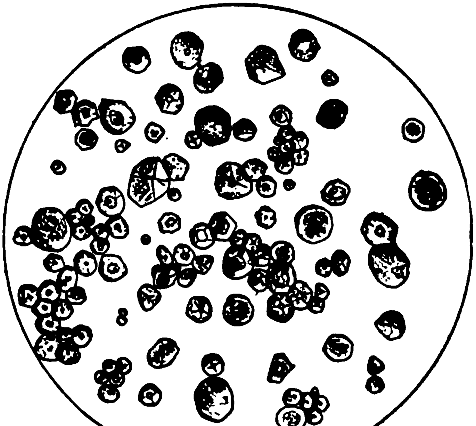

Fig. 28.

Class V.—*Rice* (Fig. 27). The granules of this starch are the smallest of all the commercial starches, and are pentagonal or hexagonal in form. Hilum extremely minute, but distinct with a very high power.

Maize (Fig. 28). The granules are polygonal, but approaching to circular, and are intermediate in size and general appearance between the starch granules of wheat and oats. The hilum is central and stellate.

Oat (Fig. 29). The granules are triangular to hexagonal in form. Both rings and hilum are invisible except under very high powers.

For illustrations of various other forms of starch granules, see under 'Starch' in Payen's Chimie Industrielle.

35. *Estimation of starch.* Various methods have been proposed and described for the determination of starch in different substances, both as raw materials and products of manufacture. As the conditions under which starch occurs in such substances vary so much, it naturally follows that one and the same method cannot be applied for its estimation in all cases, but the same general principle applies to all—viz. the extraction of the starch, either in a state of purity or after its decomposition into dextrin and maltose, or into dextrin, maltose, and dextrose, then estimating the amount of these starch products by one of the methods given under *Sugar analysis*, art. Sugar.

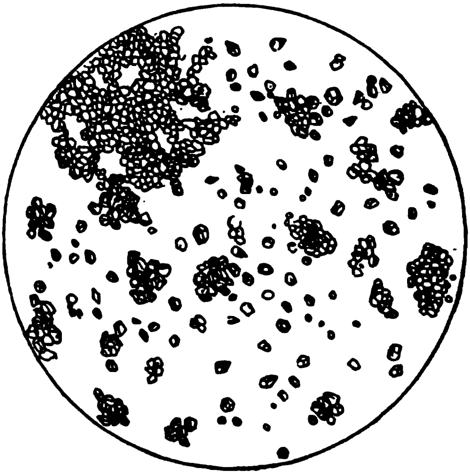

Fig. 29.

Several methods have been proposed for the direct estimation of starch—such as precipitation with solution of iodine, barium hydroxide—but none of these methods can be said to have yielded, up to the present, sufficiently trustworthy results, and the method of indirect estimation must be regarded as the only one approaching to accuracy. According to this, the starch in the substance under examination is brought into a state of solution, either as soluble starch, or as dextrin and cupric reducing sugars, by heating the substance for a certain time with glycerin, acid or diastase solution, and after filtration either carrying the process of decomposition further, or estimating the starch products first formed.

The most general process employed for the estimation of starch consists in the conversion of starch into dextrose by boiling with dilute acid (2 p.c. or more) for some hours, either with or without pressure, and estimating the dextrose by means of Fehling's solution. This process, even when most carefully conducted, is incapable of yielding anything like accurate results, these invariably coming out too low; on the one hand from the incomplete conversion to dextrose, on the other through overconversion, giving rise to condensation products having a much less or no cupric-reducing power.

A method giving fairly good results is obtained by boiling the starch with dilute acid for about half an hour to one hour, or until iodine solution shows the disappearance of starch, and then estimating the products of decomposition.

Twenty-five grms. of the substance are placed in a beaker, and heated on the water-bath with about 200 c.c. water containing 2 c.c. of strong hydrochloric acid, stirring occasionally, for about one hour. The solution is then cooled down to the normal temperature, transferred to a 250 c.c. flask, the beaker washed out two or three times with water, and the washings added to the liquid in the flask until it is made up to the containing mark at 15·5°. The whole is then well shaken and filtered, and the sp.gr. taken. The same quantity of acid as was taken for the conversion is introduced into a 250 c.c. flask, and diluted with water to the containing mark, the sp.gr. of this deducted from the sp.gr. of the starch conversion gives the sp.gr. due to the starch products, the resulting dextrin, maltose, and dextrose being estimated in the usual way.[1]

The method adopted by the A.O.A.C.[2] is as follows: 3 grms. of the material are extracted with 50 c.c. of cold water for an hour with frequent stirring. The residue is collected on a filter and washed with water sufficient to bring the filtrate up to 250 c.c. If the solution is difficult to filter, 2 c.c. of alumina cream are added. The soluble carbohydrates are determined in the filtrate both before and after inversion.

The insoluble residue is heated for 2¼ hours with 200 c.c. of water and 20 c.c. hydrochloric acid (sp.gr. 1·125) in a flask with a reflux condenser, the mixture cooled, nearly neutralised with sodium carbonate or sodium hydroxide, made up to 250 c.c., filtered and the dextrose determined in an aliquot portion of the filtrate, a correction being made for the soluble carbohydrate originally present. The weight of dextrose, multiplied by 0·9, gives the weight of starch.

For the estimation of starch in all the cereals, raw as well as malted, the method recommended by O'Sullivan (Chem. Soc. Trans. 45, 1) is undoubtedly the most trustworthy, and is carried out in the following manner:—

A fair sample of the grain is taken, and of this 5·1 grms. are weighed roughly, and ground fine in a coffee-mill, kept clean for the purpose. Of the finely-ground flour, 5 grms. or thereabouts, accurately weighed, are introduced into a wide-necked flask, capable of holding 100 to 120 c.c. The flour is just saturated with alcohol, sp.gr. 0·82, and then 20 to 25 c.c. ether added. The flask is corked and put aside for a few hours, the deposit being shaken occasionally. The clear ethereal solution is decanted through a filter, and the residue washed by decantation with three or four fresh quantities of ether, the washings being passed through the filter. To the residue 80 to 90 c.c. alcohol, sp.gr. 0·90, are added, and the mixture kept at 35°–38° for a few hours, with occasional shaking. The alcoholic solution, when clear, is decanted through the filter used in filtering the ether solution, and the residue washed a few times by decantation with alcohol, of the strength and at the temperature indicated. The residue in the flask, and any little that may have been decanted on the filter, is then washed with water into a beaker capable of holding half a litre, and the beaker nearly filled with water. In about 24 hours the supernatant liquid becomes clear, when it can be gradually decanted through a filter. The solution filters bright, but in the case of barley and oats exceedingly slowly at times; the malted grains, as well as wheat, rye, maize, and rice, yield solutions requiring no excessive time to filter. The residue is repeatedly washed with water at 35°–38°, but even this treatment does not completely free barley and oats from *a*-amylan, which dissolves with the greatest difficulty at this temperature. The residue is then transferred to a 100 c.c. beaker, and the portion adhering to the filter washed by opening the filter paper on a glass plate, and removing every particle by means of a camel's-hair brush, cut short, and a fine-spouted washbottle. When the transference is completed, the beaker, which should not now contain more than 40 to 45 c.c. of liquid, is boiled for a few minutes in the water-bath, care being taken to stir well when the starch is gelatinising, to prevent 'balling' or unequal gelatinisation. After this the beaker, still in the bath, is cooled to 62°–63°, and 0·025 to 0·35 grm. diastase, dissolved in a few c.c. of water, added. A trace of the solution ceases in a short time to give a blue colour with iodine, the starch being completely decomposed and dissolved. Yet it is well to continue the digestion at 62°–63° for an hour, as the solution, as a rule, filters better. At the end of that time the contents of the beaker are boiled for 8 or 10 minutes, thrown on to a filter, and the filtrate received in a 100 c.c. measuring flask. The residue is carefully washed with successive small quantities of boiling water. When the flask is nearly full its contents are cooled to 15·5°, and made up to 100 c.c. with water at that temperature. If care be not taken to use small portions of water at a time during the washing, the filtrate may exceed 100 c.c. before the residue is perfectly free from soluble matter; in this case the solution must be evaporated to less than 100 c.c., and then made up to that bulk after cooling to 15·5°.

Treatment with ether frees the grain from fat, &c., alcohol of 0·90 sp.gr. removes the sugars, the proteids other than casein, &c., and water at 35°–38° is intended to dissolve the amylans, &c., whilst the diastase is made to act on the residue at the temperature and under the conditions under which it dissolves starch. The 100 c.c. solution contains therefore, the products

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[1] This method always gives results which are too high, due to a small portion of cellulose becoming converted during the digestion with acid, but as this also happens in the manufacturing process a fair idea may be obtained of the quantity of commercial glucose obtainable.

[2] Association of Official Agricultural Chemists, U.S.A.

of the transformation or decomposition of the substance.

The A.O.A.C. modifies O'Sullivan's method as follows: Extract 3 grms. of the finely powdered substance on a hardened filter with five successive portions of 10 c.c. of ether, wash with 150 c.c. of 10 p.c. alcohol and then with a little strong alcohol. Place the residue in a beaker with 50 c.c. of water, immerse the beaker in a boiling water bath and stir the contents constantly for 15 mins. or until all of the starch is gelatinised; cool to 55°, add from 20 to 40 c.c. of malt extract and maintain at this temperature until a microscopic examination of the residue with iodine reveals no starch. Cool, make up directly to 250 c.c. and filter. Place 200 c.c. of the filtrate in a flask with 20 c.c. of 25 p.c. hydrochloric acid (sp.gr. 1·125), connect with a reflux condenser and heat in a boiling water bath for 2½ hours; nearly neutralise while hot with sodium carbonate and make up to 500 c.c. Mix the solution well, pour through a dry filter and determine the dextrose in an aliquot portion. Convert the dextrose into starch by the factor 0·90.

Prepare the malt extract by digesting 10 grms. of fresh finely ground malt 2 or 3 hours at ordinary temperature with 200 c.c. of water and filtering bright. Ascertain the amount of dextrose in a given quantity of the filtrate after boiling with acid, &c., as in the starch determination, and make the proper correction.

The methods of estimating starch in cereals have been fully investigated in the Guinness Research Laboratory (Trans. Guinness Research Lab. 1903, 1, 79) under the direction of H. T. Brown, and they recommend a modification of O'Sullivan's method, in which they have reduced the time required for the estimation to 5 hours. The details given are as follows: 5 grms. of the very finely ground grain are weighed out into a paper thimble and placed in the extraction apparatus, the moisture being determined on another portion of the ground material. The extractor recommended is essentially Soxhlet's form, but the wide vapour tube is connected with the top of the condenser tube so that the course of the condensed vapour is always downwards. The vessel for boiling the solvent is a thin round-bottomed Erlenmeyer flask, made of copper. The condenser has a second tube which affords additional condensing surface and also serves to keep the system under normal pressure. Eighty c.c. of alcohol of sp.gr. 0·920 are introduced into the copper flask, and the working of the apparatus adjusted so that the barley in the thimble is washed with alcohol of sp.gr. 0·900 for 3 hours (malt requires about 9 hours' washing, owing to the higher content of reducing sugars), when the whole of the reducing substances and alcohol-soluble nitrogen compounds are removed.

The contents of the thimble are now transferred to a beaker containing about 100 c.c. of water, and the whole thoroughly boiled. After cooling to 57°, 10 c.c. of an active malt-extract are added and the conversion is allowed to proceed for 60 mins. The solution is then boiled, filtered into a 200 c.c. flask, the residue well washed, and the volume adjusted after cooling. The cupric oxide reduction of the solution is determined and the maltose calculated, after correction for the reduction due to the malt extract.

In calculating the starch, the authors take advantage of the fact that when starch is hydrolised by active diastase under suitable conditions, there is a well-defined resting stage which closely approximates to the 'No. 8 equation' of Brown and Heron (*l.c.*, p. 161), and which shows 100 parts of starch yielding 84·4 p.c. of maltose. The starch equivalent of the maltose determined in the solution is thus ascertained, on the assumption, if the conditions of the theoretical equation have been complied with, that 84·4 parts of maltose correspond to 100 parts of starch.

They summarise the chief precautions to be taken in carrying out this process as follows:

It is necessary to grind the sample as fine as possible.

The extraction of the reducing substances with alcohol must not be less than 3 hours for barley and 7 hours for malt.

The converting power of the malt extract must always be determined with all possible accuracy and under the usual conditions. A malt should be chosen which has been dried on the kiln at 50°–52°, and has a diastatic power of 80 Lintner.

Another method, originally proposed by Dubrunfaut and modified by Lintner, Ewers and others, which is largely made use of, consists in the conversion of the starch in the cereal into the soluble form by treating with strong acid in the cold and estimation from the optical activity of the solution. This method, which gives very good results, has the advantage of being less troublesome than the previous methods and of requiring a much shorter time to accomplish. The method proposed by C. J. Lintner is as follows: 5 grms. of the cereal previously reduced to the finest possible state of division are triturated in a mortar with 20 c.c. of water until no lumps remain; 40 c.c. of hydrochloric acid of sp.gr. 1·15 are then added, with continued trituration, in portions of about 5 c.c. at a time, and the mixture allowed to stand for about 10 mins. The liquid is then washed into a 200 c.c. calibrated flask by means of hydrochloric acid of sp.gr. 1·1; 10 c.c. of a 4 p.c. solution of phosphotungstic acid are added to precipitate the proteins, and the volume made up to 200 c.c. with the diluted acid. After mixing, the contents of the flask are transferred to a wide-necked, stoppered bottle, thoroughly shaken and filtered. The clear filtrate is examined by the polarimeter in a 200 m.m. tube.

The concentration of the soluble starch is calculated on the basis of $[\alpha]_{\mathrm{D}}=200{\cdot}3^\circ$ for barley starch dissolved in hydrochloric acid at 20°. Provided the liquid be not allowed to remain longer than 2 hours before polarising, no decrease in the rotatory power need be feared. The method gives results 4 to 6 p.c. lower than the acid conversion process owing to the pentosans, &c., being counted in the latter process.

Wenglein (Z. ges. Brauw. 1908, 31, 53) proposes the substitution of sulphuric acid of sp.gr. 1·70 for hydrochloric acid in Lintner's process, and washes with acid of sp.gr. 1·30. The method of procedure is otherwise the same, but the solutions can be kept 8 hours unchanged before polarisation. For starch in sulphuric acid, the $[\alpha]_D = 191 \cdot 7°$.

The above methods neglect the optical activity due to constituents other than starch in the material under examination. Where these other constituents are present in appreciable quantities, correct results will not be obtained, and Ewer proposes a method in which allowance is made for this error, which is as follows:

25 c.c. of glacial acetic acid are run into a 200 c.c. flask without wetting the neck. Five grms. of the finely ground material are then added and the flask closed and vigorously shaken until the mixture is uniform. The stopper and neck of the flask are then washed down with a further 20 c.c. of glacial acetic acid and the flask placed in a boiling water bath for 10 minutes; 10 c.c. of dilute hydrochloric acid (1 in 10) are added, and the flask is left in the water bath for exactly six minutes, being shaken round every minute. Hot water is then added to make the volume up to 180 c.c. and the mixture is heated for a further 18 minutes in the boiling water bath. The solution is finally cooled, clarified by the addition of 2·5 c.c. of potassium ferrocyanide, made up to the mark with water, filtered and polarised. If the filtrate cannot be obtained clear, a few crystals of zinc sulphate can be added to assist clarification.

A blank experiment is then made to correct for the optically active bodies other than starch; this is conducted as follows: 5 grms. of the finely ground material are transferred to a 100 c.c. flask with 70 c.c. of water at about 50°, and the whole thoroughly mixed by vigorous shaking. This is digested at the ordinary temperature for one hour, then 25 c.c. of glacial acetic acid are added and the digestion continued at the same temperature for half an hour, during which the temperature is adjusted to 15·5°, the ferrocyanide added as before, and the liquid made up to the 100 c.c. mark, mixed, filtered and polarised.

For manufacturing purposes, the mere determination of the total amount of starch in a sample of grain is of little value, as no distinction is made between the insoluble and soluble starch, the latter being useless if the grain is to be used for making starch. Also the amount of gluten seriously affects the quantity of starch obtainable from the grain, for which allowance must be made in valuing the sample. According to Schreib (Zeitsch. f. Chem. 1888, 24), each part of gluten in rice causes the loss of an equal quantity of starch in the course of manufacture; consequently, a sample of rice containing 78 p.c. of starch and 4 p.c. of gluten would be more valuable than a sample containing 80 p.c. of starch and 8 p.c. of gluten, as 74 p.c. of starch could be obtained from the former, and only 72 p.c. from the latter (the yield being found by deducting the percentage of gluten from the total starch in the sample). In the case of wheat the gluten is a valuable byproduct, but in rice it is so difficult to separate from the starch—and when separated can only be sold for cattle-feeding or manurial purposes—that the less gluten the rice contains the more valuable it is. Schreib prefers, in making an analysis of 'broken rice,' to estimate the gluten, ash, and moisture, and determine the starch by difference, after making a fixed allowance for the other non-starchy constituents of the grain—that is, fat, sugar, gum, and cellulose. The whole analysis by this method can be finished in 4 hours, or considerably less time than is required for a direct estimation of the starch by the methods already given.

The starch in potatos is estimated in a rough and ready manner by ascertaining the specific gravity of the tuber. Five kilograms of potatos freed from dirt are taken and weighed in water. The weight in water divided into the original weight in air gives the specific gravity. The specific gravity ranges from 1·08 to 1·15, the heaviest potatos containing most starch and most dry matter. Tables have been drawn up by Behrend, Märcker and Morgen for ascertaining the percentage of starch from the specific gravity of the potato tuber, which give results accurate within 2 p.c.

Several varieties of starch are largely used in the adulteration of cocoa and chocolate, sago being frequently employed for this purpose; but, owing to the variable amount of starch in cocoa beans, a chemical analysis of the supposed adulterated article cannot be regarded as decisive, unless the percentage of starch found amounts to more than 10 p.c. In such cases it is advisable to resort to microscopical examination, and for this purpose the chocolate is best deprived of its fat and sugar before being placed under the microscope. The following method of examination is recommended by Hartwich (Chem. Zeit. 12, 375). The number of starch granules (which may be stained with iodine solution if advisable) in each field is counted, and a mean taken; a pure chocolate is then mixed with a corresponding amount of the supposed foreign starch, and examined in the same manner. In this way the quantity of starch added as an adulterant may be estimated with sufficient accuracy.

For estimation of starch in fodder, Leclerc (J. Pharm. Chim. [v.] 21, 641) gives the following method: 5 grms. of straw, hay, &c., are placed in a 250 c.c. flask, 10 c.c. of water added, and shaken about until every particle of the substance under examination is thoroughly moistened. 180 c.c. of a neutral zinc chloride solution, sp.gr. 1·450, are next added, and the whole heated in a salt-water bath at 108° for 1½ hours. The flask is then taken out and cooled down, and the volume made up with zinc chloride solution to 253 c.c. at normal temperature and filtered. From 25 c.c. to 100 c.c. of the filtrate is poured into a beaker containing 2 c.c. to 8 c.c. of hydrochloric acid and a sufficient quantity of 95 p.c. alcohol added to precipitate the whole of the dextrin and starch. After 24 hours the precipitate is collected on a tared filter and washed with 90 p.c. alcohol containing 0·5 p.c. hydrochloric acid until free from zinc chloride. The acid is then washed out with alcohol alone, and the precipitate weighed, then burnt, and the weight of the ash, of which there is usually a little, being carried down by the alcohol with the starch, deducted.

Starch is of very general occurrence in paper, and may be very easily detected by moistening the latter with a dilute solution of iodine, the intensity of the violet to blue colouration often forming the only means employed to ascertain the quantity of starch present. For the quantitative estimation of it Würster (Dingl. poly. J. 229, 538) proceeds as follows. The quantity of water present is first estimated, then the resin, by boiling out with alcohol, drying the paper, and weighing. The starch is next dissolved out by boiling the paper for some time with a mixture of equal parts of water and alcohol, to which a few drops of hydrochloric acid are added, and drying and weighing the residual paper; but, since the acid causes a certain loss in mineral constituents, the ash must be determined in the paper before and after extraction, and the difference deducted from the result. The following p.c. results were obtained on analysis by this method :—

Paper	Water	Resin	Starch	Ash	Fibre and cellulose by difference
Fine post, thin . .	7·2	2·9	3·5	1·8	84·6
Fine post, medium .	7·6	5·4	3·1	1·9	82·0
Fine post, strong .	7·2	3·4	3·7	7·8	77·9
Common writing paper	5·8	3·9	9·1	33·4	47·8

The starch met with in commerce and used for laundry and manufacturing purposes is almost exclusively derived from rice, maize, and potatos, and generally contains very little or no impurities. These, when they do occur, consist of vegetable fibre, gluten, or albuminoid matter, remains of pulp water, and other mineral matters. Fibre gets into the finished starch owing to imperfect arrangement of the sieves. Remains of pulp water in starch are owing to bad washing, whilst the presence of sand and other mineral matter may be due to the mixing of that portion of the starch which settles in the washing tanks next to the axis of the stirring apparatus, with the bulk of the starch—or to addition as an adulterant.

The quantity of mineral matter in starch should not exceed 0·5 p.c. When it is more than this, mineral matter, frequently barium or calcium sulphate, has been added; or the starch has been carelessly washed and not properly purified—in this case the other impurities will also be high.

As has already been stated, the proportion of moisture in ordinary air-dried starch averages about 18 p.c. It may be determined by drying the starch *in vacuo* over sulphuric acid, and finishing off in a current of dry air at 100°, the temperature being very gradually raised to this point. If the starch is at all acid, this must be neutralised by moistening it with a few drops of very dilute ammonia.

J. H. Hoffman (Woch. für Brauerei, 1903, 31) proposes a method in which the starchy matter is heated to drive out the water, which is collected and measured. Fifty grms. of starch are immersed in 400 c.c. of oil of turpentine and 10 c.c. of toluene in a vessel and heated, first at 50°, then to 140°, and finally to 155°, for 5 minutes in each case. The water formed is collected and measured, a correction of 0·2 c.c. added and the whole multiplied by 2 to give the percentage of water in the starch.

For the estimation of water in potato starch, Saare (Chem. Zeit. 52, 934) has worked out a method which combines rapidity of execution with sufficient accuracy for technical purposes. 100 grms. of the starch are rinsed into a tared 250 c.c. flask, which is then filled up to the mark with water at 17·5° and weighed; the weight of the empty flask is now deducted from this, and the percentage of water corresponding to the difference found from the following table :—

Weight found	Water p.c.	Weight found	Water p.c.
289·40	0	277·20	31
289·00	1	276·80	32
288·60	2	276·40	33
288·20	3	276·00	34
287·80	4	275·60	35
287·40	5	275·20	36
287·05	6	274·80	37
286·65	7	274·40	38
286·25	8	274·05	39
285·85	9	273·65	40
285·45	10	273·25	41
285·05	11	272·85	42
284·65	12	272·45	43
284·25	13	272·05	44
283·90	14	271·70	45
283·50	15	271·30	46
283·10	16	270·90	47
282·70	17	270·50	48
282·30	18	270·10	49
281·90	19	269·70	50
281·50	20	269·30	51
281·10	21	268·90	52
280·75	22	268·50	53
280·35	23	268·10	54
279·95	24	267·75	55
279·55	25	267·35	56
279·15	26	266·95	57
278·75	27	266·55	58
278·35	28	266·15	59
278·00	29	265·75	60
277·60	30		

The results obtained are correct to 0·5 p.c. The method may also be applied to the estimation of the water in 'green' starch, and may be used for testing the progress of the drying process in the drying chambers.

The following rule may be employed in the place of the above table.

From the weight of starch and water contained in the bottle subtract 250 and divide the difference by 0·3987, when the quotient will be the percentage of starch in the sample.

It may be more generally expressed :—

$$\frac{\text{contents of bottle in grms.}\ \textit{minus}\ \text{capacity of bottle in c.c.}}{0{\cdot}3897}=\text{grms. of anhydrous starch in weight of sample taken.}$$

J. H. and H. H.

STARCH GUM *v.* DEXTRIN.

STEAM. When water, by the agency of heat—or otherwise,—has so far changed its state as to become a compressible fluid, it is known as *steam*.

To produce steam for the purpose of performing work by its agency, water must be submitted to the action of heat until that temperature is reached at which the change from liquid to vapour is realised. This temperature, which is generally known as the 'boiling-point,' is variable, and dependent on external conditions; namely, the pressure on the surface of the liquid. At any particular pressure there is one temperature, and one only, at which steam and water can exist in equilibrium with one another.

In effecting this change of state a quantity of heat is absorbed without any rise of temperature. This is known as 'the latent heat of vaporisation,' or, more commonly, in the case of water, as 'the latent heat of steam.'

At 100° and 760 mm. pressure the quantity of heat absorbed in changing 1 grm. of water to 1 grm. of steam is 536·5 therms. As the pressure is increased, so the boiling-point rises, and the latent heat absorbed in the change diminishes. Values of the boiling-point and latent heat corresponding to temperatures are given in the 'steam table' quoted.

The following formulæ, showing the relations between temperature, pressure, and latent heat may be given, without going into the reasoning on which they are based, which is somewhat outside the scope of this article.

(α) Regnault's formula—

$$L_t = 606{\cdot}5 - 0{\cdot}695t$$

where L_t = latent heat at temperature t.

(β) The latent heat equation—

$$dT = \frac{T(v_2 - v_1)dp}{L \cdot J}$$

where L = latent heat; J = Joule's equivalent; v_2 = volume of 1 grm. of steam at temperature T; v_1 = volume of 1 grm. of water at temperature T; T = absolute temperature; dp = small increase in pressure (dynes); dT = corresponding change in temperature.

The pressure and boiling-point of a liquid cannot be raised indefinitely. If a quantity of water is heated in a sealed tube of strong glass, it is found that upon reaching a certain temperature the 'meniscus'—or surface differentiating the liquid from the vapour—disappears, and the contents of the tube become homogeneous. For water this temperature is 362°. Above this temperature steam *cannot* be converted into water, no matter how high the pressure to which it is subjected. This is known as the *critical temperature.*

The existence of such a temperature can be proved from theoretical considerations, and by the use of Van der Waal's equation—based upon the kinetic theory of gases—its value can be ascertained. Such proof, however, need not be considered here.

Entropy. The entropy is that function of the conditions of a body, such that, if it change from a value A to a value B, reversibly—

$$(B - A) = \int_A^B \frac{dH}{\theta}$$

Let a gram of water undergo a small increase of temperature dT at temperature T. Then heat absorbed $= \sigma \cdot dT$ (where σ = specific heat).

With water $\sigma = 1$. Therefore heat absorbed $= dT$.

The temperature at which this heat is absorbed is T. Therefore increase in entropy $= \frac{dT}{T}$.

And change in entropy when the liquid is heated from T_2 to T_1

$$= \int_{T_2}^{T_1} \frac{dT}{T} = \log \frac{T_1}{T_2}$$

If $T_2 = 273°$ abs. and entropy at this temperature is taken as zero, then entropy $= \log \frac{T_1}{273}$.

At the boiling-point of water under atmospheric pressure the entropy of 1 grm. of *water* $= \log \frac{373}{273}$.

Let this be converted into steam at the same temperature, the increase in entropy $= \frac{536{\cdot}5}{373}$.

Therefore the entropy of 1 grm. of *steam* at $100° = \log \frac{373}{273} + \frac{536{\cdot}5}{373}$.

The 'θ–ϕ' diagram. The relations between entropy and temperature as water is converted into steam may be represented in diagrammatic form. It is usual to take the values of the entropy as abscissæ and the values of the temperature as ordinates. The temperature is represented by the symbol 'θ' and the entropy by 'ϕ.'

In this way two curves may be plotted. One the entropy curve for water and the other the entropy curve for steam. The *area,* included between such entropy-temperature curves representing a complete cycle, gives a measure of the *heat* put into the system and that taken out. Wherefore the entropy-temperature diagram is very useful as a means of obtaining absolute values of heat efficiencies.

The increase of entropy in the case of *superheated* steam is given by the formula—

$$\text{Increase in entropy} = \sigma \int_{T_2}^{T_1} \frac{dT}{T} = \sigma \log \frac{T_1}{T_2}$$

where σ = specific heat of superheated steam.

In all entropy-temperature diagrams, *adiabatic* changes are represented by vertical lines, since, during an adiabatic change the entropy is constant in value, *i.e.* the change is 'isentropic.' Isothermal changes are represented by horizontal lines.

Velocity of steam. The velocity acquired by steam upon adiabatic expansion from a nozzle has become a matter of much importance owing to the development of the steam turbine. The velocity is obtained as follows:—

$$\text{The velocity, } v = \sqrt{2g \cdot J \cdot W} = 223{\cdot}8\sqrt{W},$$

where g = acceleration of gravity, J = Joule's equivalent, and W=work done. And the work done (in ft.-lbs.)

$$=J\left\{(T_1-T_2)\left(1+\frac{L_1}{T_1}\right)-T_2\log\frac{T_1}{T_2}\right\}$$

for initially dry steam, or

$$=J\left\{(T_1-T_2)\left(1+\frac{x_1L_1}{T_1}\right)-T_2\log\frac{T_1}{T_2}\right\}$$

for wet steam, or

$$=J\left\{(T_1-T_2)\left(1+\frac{L_1}{T_1}\right)-T_2\log\frac{T_1}{T_2}+C_p(T_s-T_1)\right.$$
$$\left.-C_p(\log T_s-\log T_1)T_2\right\}$$

for superheated steam; where J=Joule's equivalent; T_1=initial saturation temperature of steam (absolute); T_s=initial superheat temperature of steam (absolute); T_2=final temperature of steam after expansion (absolute); L_1=latent heat at temperature T_1; x_1='dryness' of the steam; C_p=specific heat of superheated steam at constant pressure.

The quantity of heat required to convert 1 lb. of water into steam, from an open vessel, or at atmospheric pressure, is 1146·1 units − F°, as given in the third column of the table (p. 193) of the properties of saturated steam.

In a closed vessel, such as a steam boiler, the temperature at which steam is produced differs with different pressures (*see* Table, p. 193). The total quantity of heat required to convert 1 lb. of water into steam is very nearly the same at all pressures (*see* Table).

In Fig. 1 let A be the cylinder of a steam engine, and *b* the piston, and let the piston occupy the dotted position *c*. Now let steam at 40 lbs. pressure per square inch above the atmosphere, or 54·7 lbs. absolute (40+14·7), be admitted behind the piston, and let the admission be continued till the piston arrives at *d*; then let the steam supply be stopped. The piston can then make no further movement except by virtue of the expansive force of the steam. Assume the piston to have moved to the position *b*, or four times as far from the end of the cylinder as the point *d*, where the steam supply was stopped; the steam in the cylinder will then have been expanded to four times its former volume.

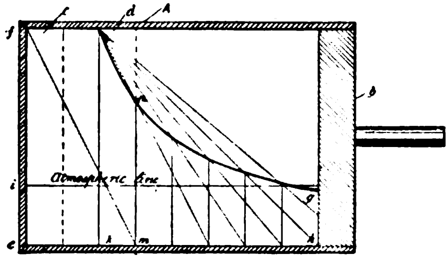

FIG. 1.

Now if we select a scale on which the height from *e* to *f* represents 54·7 lbs., and make *ei* equal to 14·7 lbs., we shall then be able to complete the figure *e, f, d, g, h, e*, the area of which represents the total force exerted by the steam on the piston, the ordinates of the curve representing on the scale the pressures at the different points occupied by the piston in its movement.

We have assumed the steam to have now expanded to four times its former volume; its pressure will then be $\frac{54\cdot7}{4}=13\cdot67$ lbs.

To find the pressure at any point between *d* and *g*, draw the line *kd*, parallel to *ef* and perpendicular to *eh*; then take any point *m*, making *mn* parallel to *kd*; join *fm*, and draw *dn* parallel to *fm*. The point *n* is a point in the curve of pressures, and *mn* represents on the scale the pressure of the steam when the piston was at that point. All other points in the curve *dng* can be determined in the same way.

The average pressure of the steam diagram, *e, f, d, g, h, e* may be calculated thus:

Let R=the ratio of expansion; H, the hyperbolic log. of the number expressing that ratio; P, the initial pressure of the steam; *p*, the mean pressure—then

$$p=\mathrm{P}\frac{1+\mathrm{H}}{\mathrm{R}}.$$

Taking the example before us

$$\mathrm{R}=4,\ \mathrm{H}=1\cdot386,\ \mathrm{P}=54\cdot7;$$

then $54\cdot7\frac{1+1\cdot386}{4}=32\cdot6$ lbs. mean pressure.

We have assumed that the pressure of steam has been fully utilised down to the line *e, h*, or line of no pressure or perfect vacuum. In practice this is not realised, and the bottom line of the actual steam diagram is generally 2 lbs. above that of a perfect vacuum; the real mean pressure would therefore be not 32·6 lbs., but 30·6 lbs. We have assumed the expansion to be isothermal. It is not so, and the practical effect of the conducting power of the cylinder is, that during the former part of the stroke of the piston, steam is being condensed in the cylinder, and during the latter part it is being re-evaporated.

Steam diagrams.

We get our knowledge of what actually takes place in a steam-engine cylinder from the indicator. This instrument is illustrated by Fig. 2. It consists of a drum *a* (on which is fastened a sheet of paper) made to oscillate backward and forward on its axis by means of a cord connection *b* to a moving part of the engine, having the motion of the piston on a reduced scale. At the side of the drum is placed a small cylinder *c* having a piston held down against the steam pressure by a spring of known tension. Let the piston be 1 square in. in area, and the tension of the spring 30 lbs. to the inch; then a pencil attached to the piston would indicate by its position the pressure of steam on the piston, at a scale of 30 lbs. per square inch.

The pencil is made to mark a horizontal line on the paper before the steam is turned on to the indicator piston; that line is termed the atmospheric line, as it indicates the pressure of the atmosphere. The indicator being attached to one end of a steam cylinder by means of a pipe, and the drum being made to turn by the engine, the pencil is caused to describe a figure on the paper of the drum like that on Fig. 3, in which the horizontal length represents the stroke of the engine on a reduced scale, and the vertical height the pressure of steam in the cylinder at all parts of the engine stroke. It is evident that the area of the figure represents the total force exerted behind the engine piston, and the average height of the diagram the average pressure of steam during that stroke. The average height—or, in other words, the average pressure—is obtained by the ordinary method of measuring irregular figures..

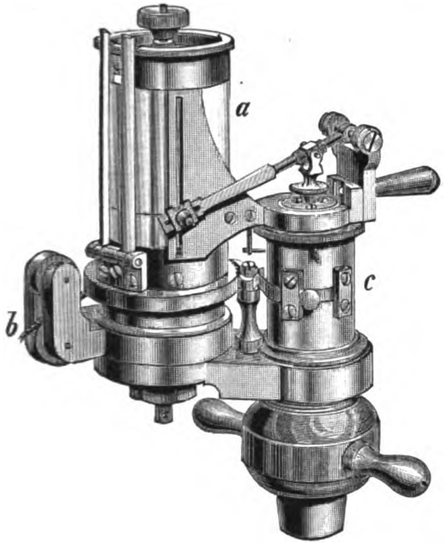

FIG. 2.

Fig. 3 represents an actual indicator diagram.

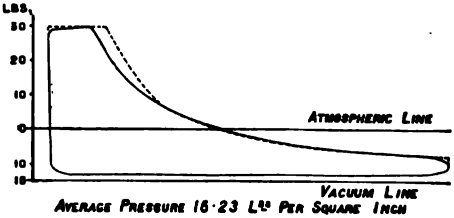

FIG. 3.

One horse-power equals 33,000 ft.-lbs. per minute. Steam engines are of various types. Single cylinder in which the steam is expanded in one cylinder only, compound engines with two, and triple expansion engines with three cylinders. The modern triple engine receives steam at 150–200 lbs. pressure per square inch, and expands it to about 6 lbs., the consumption of steam being from 12 to 10 lbs. per I.H.P. per hour, with a heat efficiency of from 15 to 20 p.c.

The best examples of steam boilers give a heat efficiency of from 60 to 80 p.c., and evaporate from 8 to 10 lbs. of water per lb. of good coal. The combined heat efficiency of engine and boiler is from 9 to 16 p.c. in the best examples of condensing engines.

PROPERTIES OF SATURATED STEAM.

Total pressure per sq. in.	Temperature in Fahr. degrees	Total heat, in Fahr. degrees from water at 32°F.	Latent heat, Fahr. degrees	Density, or weight of one cubic foot	Volume of one pound of steam	Relative volume, or cubic feet of steam from one cubic foot of water
lbs.	Fahr.	Fahr.	Fahr.	lbs.	Cubic feet	Rel. vol.
1	102·1	1113·1	1044·7	0·0030	330·36	20,600
5	162·3	1131·5	1001·5	0·0138	72·66	4,530
10	193·3	1140·9	978·2	0·0264	37·84	2,360
14·7 [1]	212·0	1146·6	965·8	0·0380	26·36	1,642
20	228·0	1151·5	954·3	0·0507	19·72	1,229
25	240·1	1155·2	945·6	0·0625	15·99	996
30	250·4	1158·3	938·2	0·0743	13·46	838
35	259·3	1161·0	931·9	0·0858	11·65	726
40	267·3	1163·5	926·2	0·0974	10·27	640
45	274·4	1165·6	921·0	0·1089	9·18	572
50	281·0	1167·6	916·3	0·1202	8·31	518
55	287·1	1169·5	911·9	0·1314	7·61	474
60	292·7	1171·2	907·9	0·1425	7·01	437
65	298·0	1172·8	904·1	0·1538	6·49	405
70	302·9	1174·3	900·6	0·1648	6·07	378
75	307·5	1175·7	897·3	0·1759	5·68	353
80	312·0	1177·1	894·0	0·1869	5·35	333
85	316·1	1178·3	891·1	0·1980	5·05	314
90	320·2	1179·6	888·1	0·2089	4·79	298
95	324·1	1180·8	885·3	0·2198	4·55	283
100	327·9	1181·9	882·6	0·2307	4·33	270

H. D.

STEARIC ACID, STEARIN *v.* OILS, FIXED, AND FATS.

STEATITE. (*Speckstein*, Ger.). A compact form of the mineral talc (*q.v.*).

STEEL *v.* IRON.

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[1] Atmospheric pressure.

STEPHANITE, 'black silver-ore,' or 'brittle silver-ore.' A silver sulphantimonite

$5Ag_2S{\cdot}Sb_2S_3$ or Ag_5SbS_5,

occasionally mined as an ore of silver (Ag, 68·5 p.c.). Crystals are orthorhombic with an iron-black colour and brilliant metallic lustre. Considerable quantities of the massive mineral have been obtained from the Comstock lode in Nevada. L. J. S.

STETHAL. *See Spermaceti*, art. WAXES.

STIBICONITE Sb_2O_4,H_2O *v.* ANTIMONY.

STIBNITE, *Antimony* or *Antimony-glance.* Native antimony sulphide (Sb_2S_3), of importance as an ore of antimony. It forms blade-like or acicular, orthorhombic crystals which possess a highly perfect cleavage in one plane direction parallel to their length. Radially-fibrous and lamellar masses, with the perfect cleavage conspicuous on their broken surfaces, are of common occurrence. Sp.gr. 4·6. The colour is steel-grey with a brilliant metallic lustre, but on exposure to light the surface becomes dulled. Although often regarded as a typically opaque mineral, very thin cleavage flakes of stibnite transmit a small amount of red light (refractive indices, $\alpha=3{\cdot}194$, $\beta=4{\cdot}046$, $\gamma=4{\cdot}303$ for wave-length 760), and they are still more transparent for heat rays (A. Hutchinson, Min. Mag. 1903, 13, 342; 1907, 14, 199). Light has a remarkable effect on the electrical conductivity of crystals of stibnite: the close proximity of a strong electric arc-light causes this to increase by over 200 p.c., and when the light is removed it quickly returns to its former value (F. M. Jaeger, Zeitsch. Kryst. Min. 1907, 44, 45).

The mineral is quite soft (H.=2), and the crystals are readily bent, with the production of characteristic zigzag forms. The bending is accompanied by a slipping, along a glide-plane, of one portion of the crystal over another portion. This gives rise to fine striations running transversely across the cleavage surfaces, which being almost always present (no doubt as a result of earth pressures) render stibnite a mineral easily recognisable at a glance.

Stibnite occurs in metalliferous veins, and is found in many localities. The finest specimens (magnificent groups of brilliant, prismatic crystals reaching a length of 20 ins.) come from the Ichinokawa antimony mine, near Saijo on the Japanese island of Shikoku. Good crystals, often penetrating crystals of barytes, are well known from Felsöbánya in Hungary. As an ore of antimony stibnite is mined in several countries, the principal ones, arranged in the order of their production, being: France (Auvergne), China (prov. Hunan), Italy, Mexico, Victoria, and Hungary.

Besides being smelted as an ore of antimony, stibnite is used to a limited extent for the preparation of pure hydrogen sulphide. In the East, powdered stibnite is employed for darkening the eyebrows, and it was also used by the ancients for the same purpose, hence the old name *platyophthalmon* for this mineral.

Reference.—Chung Yu Wang, Antimony, its History, Chemistry, Mineralogy, &c., London, 1909. L. J. S.

STICK LAC *v. Lac resin*, art. RESINS.

STILBENE, *toluylene*, sym-*diphenylethylene* $C_6H_5{\cdot}CH:CH{\cdot}C_6H_5$, is formed when benzylidene chloride is heated with sodium (Limpricht, Annalen, 1866, 139, 38); by heating benzoin with zinc-dust and acetic acid (Blank, *ibid.* 1888, 248, 7); by the slow distillation of phenyl fumarate (Anschütz, Ber. 1885, 18, 1948); by the action of light on the silver salt of phenylnitromethane (Angeli, Castellana and Ferero, Chem. Zentr. 1909, [ii.] 975); on treating phenylbenzyl carbinol with dilute sulphuric acid; by heating a mixture of benzaldehyde and phenylacetic acid in a sealed tube—all of which methods indicate the above constitution.

Preparation. Stilbene is obtained in fair yields by dropping toluene into a red-hot tube containing lead oxide (Lorenz, Ber. 1874, 7, 1096); by heating benzthioaldehyde with copper powder (Klinger, *ibid.* 1877, 10, 1878), or more simply by heating benzaldehyde alone with sulphur in sealed tubes to 180°. Better results are obtained by treating deoxybenzoin with sodium ethoxide (Sudborough, Chem. Soc. Trans. 1895, 67, 604); by acting upon benzaldehyde with phenyl magnesium iodide (Klages and Heilmann, Ber. 1904, 37, 453); by the action of 10 p.c. caustic soda on phenylnitromethane at a temperature of 160°, when a 90 p.c. yield is obtained (Wislicenus and Endies, *ibid.* 1903, 36, 1194).

Properties and *reactions.* Monoclinic tables, m.p. 124°, b.p. 306°, insoluble in water, easily soluble in hot alcohol, ether, benzene, &c. On passing through a heated tube it forms toluene and phenanthrene (Graebe, *ibid.* 1873, 6, 126); on reduction with hydriodic acid it yields dibenzyl; it is oxidised by chromic anhydride to benzoic acid; heated with sulphur it forms tetraphenylthiophene; by the action of sulphuric acid it forms a disulphonic acid (Limpricht and Schwanert, Annalen, 1868, 145, 335); it is converted by ozone into an ozonide (Harries, Ber. 1903, 36, 1933); on passing nitrogen peroxide into its benzene solution it forms stilbene nitrite (Gabriel, *ibid.* 1885, 18, 2438); with picric acid it forms an insoluble picrate; by the addition of bromine in carbon disulphide solution there are produced two stereoisomeric stilbene bromides (m.p. 237° and 110°) (Wislicenus and Seeler, *ibid.* 1895, 28, 2694).

iso-*Stilbene.* From the lower melting-point stilbene bromide obtained as above, a stereoisomeric modification of stilbene may be obtained by careful reduction. As this bromide has the trans- configuration *iso*stilbene must be the trans-isomeride. It is extremely unstable, and on distillation, or under the influence of sunlight, or in presence of traces of bromine or iodine it passes immediately into ordinary stilbene, which consequently possesses the cis- configuration (Wislicenus, Chem. Zentr. 1901, [i.] 463).

o-*Dinitrostilbene* from *o*-nitrobenzyl chloride and alcoholic potash, exists in two stereoisomeric forms (m.p. 126° and 196°); on reduction they yield the same *o*-diaminostilbene (Bischoff, Ber. 1888, 21, 2072).

p-*Dinitrostilbene*, prepared in the same way, has also been isolated in two forms (m.p. 210° and 280°), which form on reduction *p*-diaminostilbene (m.p. 227°) (Strakosch, Ber. 1873, 6, 328; Walden and Kernbaum, *ibid.* 1890, 23, 1959).

Tetranitrostilbene, from tetranitrobenzyl chloride and alkali (m.p. 264°) (Kraususky, J. Russ. Phys. Chem. Soc. 27, 339).

Nitrostilbene sulphonic acids (v. Bender, Ber. 1895, 28, 422; Fischer and Hepp, *ibid.* 1895, 28, 2281; Green and Wahl, *ibid.* 1897, 30, 3100).

Stilbene colouring matters. *p*-Nitrotoluene and its *o*-substituted derivatives under the influence of alkalis yield derivatives of stilbene, which are the parent substances of numerous dyes (*see* Azo- colouring matters).

STOCKHOLM TAR. A bituminous liquid obtained from the wood of *Pinus sylvestris* (Linn.) and other species of *Pinus* by destructive distillation.

The tar exported from Stockholm in earlier times, and to which the term Stockholm tar was applied, was brought from the northern part of Sweden and from Finland, where the tar was produced by peasants from dry wood stumps burned in 'tjärdàlar,' or specially made tar-burning ground. On arrival at the Stockholm tar court all barrels were 'wrecked' before being shipped abroad. The procedure of wrecking was as follows: After the barrel had been filled with tar it was left standing for some hours, when the water which had accumulated on the surface was drawn off and the barrel refilled with tar. The 'wreckers,' who were sworn servants of the Tjärhof, issued a certificate, which at that time was required for the export, stating that the barrels contained the regulation quantity and that the tar had been 'wrecked.' The old Stockholm tar was shipped in barrels of 125 litres. Several tar exporters in the north of Sweden still use barrels which have been examined by the State Comptrollers as to their capacity, and if found to hold the right measure the barrel is stamped with three crowns. Many importers attach great importance to this mark, and erroneously look upon it as a quality mark. A variety of tars differing very much from one another are imported from Sweden. So-called Stockholm tar is generally shipped in three qualities or grades, viz.: fine thin (no grains or crystals), middle fine or ordinary (either gluey or thin and fine-grained), thick (very close-grained). The name 'Umea tar' is applied to similar tar produced in the Umea district and shipped from the port of Umea. This tar is delivered in 'Swedish barrels' containing 27½ galls. and weighing 167 kilos. gross, and 133 kilos. net. 'Umea tar' is considered the best in the market. 'Skelleftea' and 'Lulea' tar are of a similar quality. These three tars are sometimes also shipped as 'Stockholm tar.' Swedish 'factory tar'—obtained from waste wood in charcoal kilns at the saw mills, and produced as a by-product in charcoal burning—must not be confounded with 'Stockholm' or 'Umea' tar. It is easily distinguished by its colour and smell. The genuine tar is yellow-brown or light-brown in colour, and with a turpentine smell, while the factory tar is of a dark-brown or black colour with a strong smoky smell. The tar manufactured by peasants and shipped from Finland (Wasa and Uleaborg) was formerly, and is sometimes now, called 'Stockholm tar,' but is generally shipped as 'Wasa tar.'

Until comparatively recent years there were only two kinds of wood-tar regularly exported to England, viz. Stockholm tar exported from the Gulf of Bothnia, and Archangel tar from Archangel. The latter was shipped in barrels containing about 112 litres. Then the so-called Russian tar exported from Riga, Libau, and Königsberg came on the market, and has largely taken the place of 'Stockholm tar,' owing to the scarcity and high price of the latter, and also because Russian tar is obtainable at all times of the year. Disputes between buyers and sellers as to the real meaning of 'Stockholm tar' have arisen since the appearance of the cheap factory tars on the market, and British importers have suggested that the term 'Stockholm tar' should be retained for the peasant-made article, as it has been used for centuries, and for the 'factory tar' 'Swedish kiln wood-tar.' The Swedish exporters advise that buyers of tar should purchase from samples and insist on a full description of the tar. They much prefer this to a guarantee to sell 'genuine Stockholm tar.' (D. McEwan, Brit. and Col. Drug. 1911, 59, 138; J. Soc. Chem. Ind. 1911, 30, 274).

STORAX *v.* Balsams.

STOVAINE. Trade name for the hydrochloride of dimethylamino-*tert* amyl benzoate

$$(CH_3)(C_2H_5)[CH_2{\cdot}N(CH_3)_2,HCl]C{\cdot}O{\cdot}COC_6H_5,$$

obtained by acting on dimethylaminoketone with ethyl magnesium bromide; ethyl dimethylaminopentanol is thus obtained, and on treating with benzoyl chloride gives stovaine. Used as an anæsthetic (*v.* Synthetic drugs).

STOWITE *v.* Explosives.

STRAMONIUM *v.* Datura.

STRASS *v.* Gems, imitation and counterfeit.

STRAWBERRY. The fruit of *Fragaria vesca* (Linn.). Many varieties are known.

König gives as the average composition—

	Water	Protein	Invert sugar	Cane sugar	Other N-free sub.	Acidity: malic acid	Fibre	Ash
European	87·0	0·6	5·1	1·1	2·8	1·1	1·6	0·7
American	89·7	1·0	4·8	0·6	0·4	1·4	1·5	0·6

According to American investigations (Bull. 28, U.S. Dept. of Agric. 1899) about three-fourths of the total N present exists as real proteids.

The acidity of strawberries is usually stated to be due to malic acid, but according to Paris (Chem. Zeit. 1902, 26, 248) it is chiefly due to citric acid. On the other hand, Stone (Agr. Science, 1889, 257) states that citric acid can only be present in small quantities, if at all. Stone found that the ratio of acid to sugar is, in wild strawberries 1 : 2, in American varieties 1 : 3·5, and in European varieties 1 : 9.

There appears to be no doubt that American-grown strawberries are richer in protein and acid, but much poorer in total solids, sugar, and cellulose than European ones.

Strawberries contain small quantities of salicylic acid, probably in the form of an ester (Portes and Desmoulières, J. Pharm. Chim. 1901, 14, 342; also Süss, Chem. Zentr. 1903, ii. 841; and Windisch, Zeitsch. Nahr. Genussm. 1903, 6, 447), the amount found being usually about 2 or 3 mgms. per litre of juice. The fatty oil of strawberries has a sp.gr. 0·9345 at 15°/4°, saponification number 193·7, acid number 6·41, Reichert-Meissl number 2·1, iodine number (Hübl) 180·3. It yields 88·2 p.c. of insoluble fatty acids, their iodine number being 192·3 (Aparin, J. Russ. Phys. Chem. Soc. 1904, 36, 581).

Strawberry root contains a tannin, *fragarianin*, of a pale-yellow colour, soluble in water and alcohol, yielding *fragarin* when boiled with dilute hydrochloric acid (Phipson, Chem. News, 37, 135).

The flavour of strawberries is imitated in confectionery by the use of a mixture of 2 parts ethyl acetate and 1 part of amyl acetate.

Strawberries are highly valued as a fruit, and in most cases are easily digested; in the case of a few susceptible persons, however, they produce an urticaria comparable to that produced by eating shell-fish. According to Mendel and Hooker (Amer. J. Physiol. 1902, 7, 380), intravenous injections of an aqueous extract of strawberries produced an increased flow from the thoracic duct, a fall of blood pressure, and a diminution in the coagulability of the blood.

For the effect of manuring upon the yield and especially the earliness of strawberries, *v.* Dyer and Shrivell (J. Roy. Hort. Soc. 1903, 27, 4), who found that moderate dressings of phosphates and sodium nitrate, applied with a light manuring with dung, slightly increased the yield of fruit, but had a distinct influence upon early ripening, whilst potash salts had an injurious effect, diminishing the yield and retarding maturity. H. I.

STREAM-TIN *v.* Cassiterite.

STROMEYERITE. *Argento-cuprous sulphide* or *Argentiferous copper glance* AgCuS or $Ag_2S{\cdot}Cu_2S$. A mineral crystallising in trimetric forms isomorphous with copper-glance. Sectile, dark steel-grey colour, shining streak; subconchoidal fracture. H. 2·5–3·0; sp.gr. 6·2–6·3 (*v.* Copper-glance).

STRONTIANITE. Native strontium carbonate ($SrCO_3$) crystallising in the orthorhombic system and isomorphous with aragonite and witherite (*q.v.*). The mineral takes its name from Strontian in Argyllshire, where it was known in the lead mines as early as 1764, and in material from this source the element strontium was discovered. Crystals are rare and usually acicular or spiky in form; more often the mineral is found as columnar or fibrous masses. The colour is usually white or pale-yellowish, but the columnar masses from Strontian show a characteristic and delicate shade of green; sp.gr. 3·7; H. 3½. Strontianite is a mineral known in comparatively few localities, and in quantities sufficient for mining only in the neighbourhood of Münster and Hamm in Westphalia, where it forms veins in calcareous marl. It is used for the preparation of strontium hydroxide, which is employed (in preference to the poisonous barium compound) in the refining of beet-sugar. It is also used for producing the red fire of fireworks, and in the manufacture of 'basic bricks.' L. J. S.

STRONTIUM. Sym. Sr. At.wt. 87·6.

Strontium derives its name from Strontian in Argyllshire, where strontianite, the carbonate of strontium, was first found. This mineral was suspected by Crawford in 1790 to contain a new earth, the existence of which was confirmed by Hope in 1792, and by Klaproth in 1793.

All primary rocks contain strontium in greater or less quantity. More strontium than barium has been taken up by water, owing to the readier solubility of the sulphate, which is found deposited along with gypsum on evaporation. The carbonate and sulphate of strontium are often found along with deposits of common salt (Dieulafait, Ann. Chim. Phys. [v.] 15, 540).

Strontium is chiefly found as the sulphate, *celestine* $SrSO_4$, and the carbonate, *strontianite* $SrCO_3$. It almost invariably accompanies calcium in traces in the various forms of aragonite and calcite. In *barytocelestine* it occurs along with barium as a mixed sulphate; barytes also generally contain traces of strontium. *Brewsterite* $Al_2O_3{\cdot}H_4(BaSr)O_3{\cdot}(SiO_2)_6,3H_2O$ is a silicate in which strontium occurs associated with barium. Strontium, in minute traces, is present in the mineral waters of Carlsbad, Kaiser-Franzenbrunnen, and many other places, and in sea-water.

Davy obtained, by a method identical with that described under barium, a metallic body which he supposed to be strontium, but which was probably only a rich amalgam. Matthiessen, by the electrolysis of the fused chloride, obtained a metallic-looking mass, and the method was used also by Borchers (Zeitsch. Elektrochem. 8, 759) with similar results. It seems, however, probable that some action similar to that described under Barium and Calcium takes place, and that a sub-chloride and not the metal is formed. The compound has the property of decomposing water. The best method of obtaining strontium is probably that of Guntz, described under Barium. An amalgam is obtained by Davy's method, and the greater part of the mercury may be removed by distillation in a vacuum. The impure strontium so obtained is then treated with hydrogen at a red heat, whereby the hydride is formed and the last traces of mercury removed. The hydride is then decomposed by exhausting the tube and finally raising the temperature to 1100°.

Guntz does not appear to have determined the physical constants of strontium, and it is doubtful whether those given by earlier experimenters are of value. Like barium, it is a white, malleable metal. It decomposes water in the cold and unites with the halogens, sulphur, and phosphorus.

Strontium hydride SrH_2 is obtained by heating the amalgam in a current of hydrogen. The mercury distils off, leaving a white solid, which decomposes water, yielding hydrogen and the hydroxide.

Strontium monoxide, or *strontia* SrO, is obtained when the nitrate is heated to redness, or when the carbonate is ignited, either alone or in contact with carbonaceous matter, such as coal or charcoal. Leplay (Dingl. poly. J. 256, 169), having observed that in the decomposition of strontium carbonate by means of superheated steam the hydroxide so formed loses water at temperatures near its melting-point, and is converted into a solid mass of oxide, devised a process for the production of strontium oxide upon the large scale. Moist strontium carbonate, moulded into suitable forms, is deprived of a portion of its moisture and heated in retorts placed over a decomposing furnace. Superheated steam is also blown into the retorts, and the liberated carbon dioxide led away. The oxide formed by ignition of the hydroxide is removed in waggons, fresh carbonate being introduced in order to make the process continuous. Specially constructed kilns using generator gas are now usually employed for preparing the oxide by burning the carbonate at a high temperature.

Strontium oxide is a greyish-white porous mass of sp.gr. 3·9, non-volatile, infusible and glowing with a dazzling white light in the oxy-hydrogen flame. It possesses an alkaline taste and reaction. Like lime, when moistened with water, it slakes, becoming hot and falling to powder. If the calculated quantity of water be added to form the crystalline hydroxide, the whole solidifies to a solid mass.

Strontium hydroxide $Sr(OH)_2$ is the product of the action of water upon the oxide. On dissolving the hydroxide in 5–6 parts of boiling water, filtering hot and allowing to cool in a closed vessel, small transparent quadratic crystals of $Sr(OH)_2,8H_2O$ are deposited; these deliquesce in the air and are rapidly converted into carbonate. Heated to 100°, water is expelled, leaving the hydroxide $Sr(HO)_2$. This hydroxide may also be obtained in the fused state by heating the crystals to low redness, when they solidify on cooling to a greyish-white crystalline mass. At a red heat all the water is expelled, anhydrous strontia remaining. The crystals of $Sr(OH)_2,8H_2O$ are soluble in 50 parts of cold and 2·4 parts of boiling water, forming strontia-water, which rapidly absorbs carbon dioxide from the atmosphere, becoming coated with a crust of carbonate.

According to Heyer (Ber. 19, 2684), when strontium hydroxide is heated to bright redness and the oxide so formed exposed to air saturated with aqueous vapour and afterwards to dry air, a crystalline powder of the composition $Sr(OH)_2,H_2O$ is obtained. Another hydrate $Sr(HO)_2,2H_2O$ also exists according to Müller-Erzbach (Ber. 20, 1628).

Strontium hydroxide is used largely in the preparation and refining of beet-root sugar, and in the extraction of crystallisable sugar from molasses. Its use depends upon the property of the oxide and hydroxide of strontium to combine with sugar to form saccharates easily decomposable by carbon dioxide. Lime was formerly used, but strontia is preferable, the precipitated saccharate of strontia being more granular than that of lime. Scheibler shows that to obtain a good yield 3 molecules of $Sr(OH)_2$ should be employed; if 4 molecules are used 98·4 p.c. of the sugar is precipitated. For 1 kilog. of molasses ½ a kilog. of $Sr(OH)_2$ in 1½ kilogs. boiling water is a good proportion. The mixture is stirred, then, after standing nearly a day, the saccharate crystallises out; it is afterwards pressed and washed with cold strontium hydroxide solution. Under increased pressure and temperature a tribasic saccharate is obtained, but if this while hot is introduced into hot water it is decomposed, $Sr(OH)_2$ crystallising out, and the ordinary saccharate

$$C_{12}H_{22}O_{11}\cdot SrO,5H_2O$$

remaining in solution. On the large scale this clear solution is heated to over 100° when the saccharate is precipitated, impurities remaining in solution. The saccharate is afterwards decomposed by carbon dioxide.

Many processes have been devised for the manufacture of strontium hydroxide, of which the following are the most important:—

In Niewerth's process (Dingl. poly. J. 251, 191), celestine ($SrSO_4$) is mixed with equal quantities of coal and brown iron ore and roasted. On lixiviation of the product with water, strontium hydroxide and ferrous sulphide are produced.

Claus (Dingl. poly. J. 253, 82) proposes to obtain it from the chloride by addition of an equivalent of barium hydroxide to the hot solution; $Sr(OH)_2$ crystallises out and barium chloride is recovered by evaporation and crystallisation. Also by adding an equivalent of barium hydroxide to a hot solution of strontium sulphide. It is also found that if a solution of barium sulphide is added to a hot solution of strontium sulphide, strontium hydroxide crystallises out on cooling, barium hydrosulphide remaining in solution. A similar reaction occurs between sodium and strontium sulphides. On evaporating the solutions of barium or sodium hydrosulphide, mixing with coal-dust, igniting gently and lixiviating, solutions of barium and sodium sulphides are obtained which can be used again. Mother liquors containing strontium hydrosulphide when evaporated and ignited with coal-dust give strontium hydroxide on lixiviation with water. Claus also (J. Pharm. Chim. [v.] 11, 434) describes a process based on the decomposition of strontium monosulphide into hydroxide and hydrosulphide under influence of water, the hydroxide crystallising out.

Leplay's process (Dingl. poly. J. 254, 436) consists in treating strontianite ($SrCO_3$) with steam superheated to a temperature higher than the melting-point of the hydroxide. The carbonate is introduced into iron pots and there heated to low redness; the contents are then removed to retorts, into which the superheated steam is blown. The semi-fluid hydroxide flows into a suitable receiver, and is thence run off into moulds. It is best to prepare the carbonate by working it into a paste with 30–40 p.c. weak caustic lye, and converting into balls or hollow cylinders.

Knight (Eng. Pat. 16220, 1884) precipitates strontium sulphide with an equivalent of zinc chloride; after decantation from the precipitated zinc sulphide, the clear solution is decomposed with caustic soda, strontium hydroxide crystallising out on cooling.

Lee Pattinson (Eng. Pat. 16989, 1884) employs the following process: An equivalent of manganese dioxide is added to a solution of strontium sulphide and air of the temperature of 100°F. blown through. About 66 p.c. is converted into hydroxide and 33 p.c. into insoluble thiosulphate, 33 p.c. of the sulphur present being also deposited. The sulphur is extracted by naphtha, and the oxide of manganese used again. If air is blown through only until a precipitate begins to form, two-thirds of the strontium is found to be converted into hydroxide, and on crystallising almost pure hydroxide is obtained. The mother liquor containing trisulphide is converted to sulphide and used again.

Mactear (Eng. Pat. 5170, 1886) mixes strontium sulphate with slightly more than its equivalent of sodium sulphate and a quantity of carbonaceous matter. The finely-divided mixture is heated in a furnace until the sulphates become reduced to sulphides. The product is treated with hot water, when the two sulphid react, with the production of sodium hydrosulphide and strontium hydroxide, which latter is obtained by crystallisation. The mother liquor containing the former is evaporated, and the residue used again in reducing a fresh supply of celestine. The strontium hydrosulphide obtained as a by-product in the working of the Claus process may be utilised by mixing it with a solution of sodium sulphide Na_2S, when strontium hydroxide and sodium hydrosulphide are formed, the former of which may be crystallised out as usual.

According to Trachsel (J. Soc. Chem. Ind. 1886, 630) other processes for the manufacture of the hydroxide from strontianite and celestine are as follows. If the native carbonate is employed as the raw material, it is first converted into oxide in kilns, the burning requiring a higher temperature than that of lime; the resulting oxide is then dissolved in boiling water, the solution clarified and crystallised. If the sulphate is used, the process is more complicated. The powdered mineral may be boiled with a solution of sodium carbonate, and the resulting carbonate made into bricks with sawdust and calcined as above. Or a mixture of strontium sulphate and sodium carbonate may be furnaced, also yielding strontium carbonate and sodium sulphate. In a third process ammonium carbonate is used to convert the sulphate into carbonate, the conversion being accomplished in closed vessels provided with stirring apparatus.

Trachsel, in order to simplify the manufacture, has devised the following more direct process. It is based upon the fact that a solution of strontium sulphide treated with caustic soda becomes converted into strontium hydroxide, sodium sulphide or hydrosulphide being simultaneously formed

$$SrS+2NaOH=Sr(OH)_2+Na_2S$$
$$SrS+NaOH+H_2O=Sr(OH)_2+NaSH.$$

The second reaction is more advantageous, requiring only half the soda. The sodium sulphide and hydrosulphide are then converted into carbonate by a stream of carbon dioxide:

$$2NaSH+CO_2+H_2O=Na_2CO_3+2H_2S.$$

The sulphuretted hydrogen may be utilised by converting it into sulphur dioxide by passing it through a Claus kiln.

The sodium carbonate is next treated with caustic lime, obtaining thereby calcium carbonate and caustic soda, which can be used again, thus rendering the process continuous.

The sulphate fresh from the mine is passed through a crushing apparatus, mixed with 7 cwts. of coal to every 20 cwts. of sulphate, and the mixture calcined in a plus-pressure or revolving furnace, 3–4 hours being sufficient for the conversion into sulphide. It is then carried to the lixiviators, consisting of round or square vats of boiler-plate, each provided at 6 ins. from the bottom with a removable grating of iron bars, on which is spread a filter of sugar bags covered with fragments of brick or other suitable material to protect it from the red-hot furnace charge. In the centre of the grating an upright cast-iron pipe is fixed, passing through the grating but not quite touching the bottom of the vat, and bearing on the top a flat or umbrella-shaped plate, between which and the pipe an interstice is left for the escape of liquor which is forced up by the steam entering through a steam-pipe placed in the centre of the cast-iron pipe at the bottom of the vat, over which it projects several inches. In these vats the charges as they come from the furnace are covered with boiling water or weak liquor from a former operation, and the steam is turned on, which not only keeps the liquor boiling, but also circulates it energetically, forcing the liquor which has percolated through the false bottom upwards in the cast-iron pipe, when it falls back upon the charge. When the liquor has attained the strength of 24°Tw. it is allowed to settle, and then run off to crystallising tanks, where it is treated with a strong solution of caustic soda. The greater part of the strontium hydroxide falls down at once, a further quantity crystallising out on cooling. The mother liquor (chiefly NaSH) is drained away from the crystals and run into evaporating pans, where it is concentrated to 30°Tw. and again run into other crystallising tanks, where it deposits practically all its strontium hydroxide.

The crystals are dried and washed in hydro-extractors and twice re-crystallised, which renders them ready for packing. This double re-crystallisation causes serious loss, but by the following device one re-crystallisation is found sufficient. The impure hydroxide, after being once dried and washed is thrown into a muffle-furnace, where it is gently heated and stirred about. Part of the water of crystallisation is thus driven off, the iron sulphide is oxidised, and any strontium sulphide is changed to sulphite, sulphate, and thiosulphate, a little strontium carbonate being also formed. This carbonate is sufficient to precipitate all the iron when the furnace product is dissolved in boiling water. The solution is clarified and allowed to cool, and the crystals, after passing through the hydro-extractor, are ready for packing. By this means also the crystals can be produced in a shorter time, about six days being the average required.

Strontium dioxide SrO_2 is formed as a hydrate when a solution of strontium hydroxide is mixed with one of hydrogen peroxide, shining scales of the composition $SrO_2,8H_2O$ being deposited. When heated to 130°, or even in dry air at the ordinary temperature, it gives off water, and the peroxide is left in the form of a white powder. On heating this powder to redness, oxygen is evolved without fusion, strontium monoxide remaining.

Strontium chloride $SrCl_2$ is formed directly by the combustion of strontium in chlorine, or by heating anhydrous strontia in a stream of chlorine. According to Konigel-Weisberg (Ber. 12, 511) chlorine has no action on dry $Sr(OH)_2$, but it converts the hydrate $Sr(OH)_2,8H_2O$ into chloride and chlorate, a small quantity of hypochlorite being also formed. Strontium chloride is generally obtained from strontianite or celestine. The former, dissolved in hot hydrochloric acid, deposits on cooling long hexagonal deliquescent needles of $SrCl_2,6H_2O$ of sp.gr. 1·603, isomorphous with the hydrate of calcium chloride. When heated the crystals lose their water, the white anhydrous salt being left, which fuses at a high temperature, forming a glassy mass of sp.gr. 2·96. According to Mulder, 100 parts of water dissolve 44·2 parts $SrCl_2$ at

0°, 83·1 parts at 60°, and 101·9 parts at 100°. It is also soluble in alcohol.

The anhydrous chloride absorbs dry ammonia, forming a white powder of the composition $SrCl_2·8NH_3$.

Wackenroder (Dingl. poly. J. 253, 440) proposes to prepare strontium chloride on the large scale by adding an equivalent of calcium chloride to strontium sulphide obtained by the reduction of celestine, and passing carbon dioxide into the mixture, when sulphuretted hydrogen is given off and the calcium precipitated as carbonate. The filtered solution is then evaporated to the crystallising-point of the strontium chloride.

Mactear (Eng. Pat. 1915, 1886) mixes celestine and calcium chloride with charcoal or other form of carbon and a little limestone or lime, and strongly heats the mixture in a furnace. the waste fire-gases being utilised to dry the calcium chloride. The product, consisting of strontium chloride and calcium sulphide or oxysulphide, yields on lixiviation solutions from which strontium chloride can be crystallised.

Strontium oxychloride. When strontium hydroxide is boiled in a concentrated solution of strontium chloride, the liquid, on cooling, deposits nacreous lamellæ of $SrCl_2·SrO,9H_2O$, easily decomposed by water and alcohol. *In vacuô* this oxychloride loses water, becoming $SrCl_2·SrO,H_2O$ (André, Compt. rend. 93, 58).

Strontium bromide $SrBr_2$ is obtained when strontium is burnt in bromine vapour, or when the carbonate is dissolved in hydrobromic acid. From the solution, on evaporating, long needles of the hydrate $SrBr_2,6H_2O$ are obtained. It is readily soluble in water and slightly soluble in alcohol.

Strontium iodide $SrI_2,7H_2O$ is prepared by evaporating a solution of hydriodic acid saturated with strontium hydroxide. It crystallises in six-sided plates, very soluble in water. Heated in a closed vessel it may be fused without parting with iodine, but in contact with air iodine fumes are evolved, strontium oxide being left.

Strontium fluoride SrF_2 is also similarly obtained by treating the oxide or carbonate with hydrofluoric acid, or by precipitating a soluble strontium salt with sodium fluoride. Strontium fluoride is a white powder insoluble in water.

Strontium carbide SrC_2 has been prepared in the pure crystalline condition by Moissan by reducing the oxide with carbon in the electric furnace, using 120 grms. of strontia to 30 grms. of sugar carbon. The reduction is effected at a lower temperature than the corresponding calcium carbide. It is a brownish crystalline mass, density 3·19, which decomposes water yielding acetylene and strontium hydroxide.

Strontium carbonate $SrCO_3$ occurs native as strontianite in rhombic crystals, isomorphous with those of aragonite and witherite. Strontium oxide absorbs CO_2, as does CaO, when strongly heated to a temperature about 1050°, becoming incandescent, the luminosity being greater than that of lime. But the normal carbonate is never formed in this way (Raoult, Compt. rend. 92, 1110). When a solution of a strontium salt is precipitated by an alkaline carbonate, strontium carbonate is obtained as a white powder of sp.gr. 3·62 It may be obtained crystallised in the form of strontianite by fusing a mixture of potassium chloride, sodium chloride and the amorphous carbonate, and allowing to cool (Bourgeois, Bull. Soc. chim. [ii.] 37, 447). When gently heated it becomes converted into strontia. A litre of water, according to Fresenius, dissolves 55 milligrams of strontium carbonate. It is still less soluble in aqueous ammonia or ammonium carbonate, but dissolves more readily in ammonium chloride and nitrate. Boiled with ammonium chloride solution it becomes converted into strontium chloride.

Several processes have been devised, in view of the use of strontia in sugar refining, for the production of strontium carbonate on the large scale. Urquhart and Rowell (Dingl. poly. J. 1884, 252) treat native sulphate (celestine) with sulphuric acid to remove iron and aluminium, then boil the product with mixed solutions of sodium sulphate and carbonate. The resulting mixture of strontium sulphate and carbonate is heated in a furnace with excess of Na_2CO_3, and the mass lixiviated, $SrCO_3$ being thus obtained, together with a liquor which is used for the treatment of fresh celestine.

Mebus and Decastro (Dingl. poly. J. 257, 198) digest finely-pulverised strontium sulphate with a solution of ammonium carbonate, the decomposition being effected in an apparatus fitted with agitating appliances.

A basic hydrated strontium carbonate is formed when the hydrate $Sr(OH)_2,H_2O$ is exposed to a current of carbon dioxide, and the product dried at 145° (Finkener, Ber. 19, 2958).

Strontium nitride Sr_3N_2 may be obtained by the action of nitrogen on the amalgam at a red heat. The mercury distils off, leaving a dark fused mass which decomposes water with the formation of ammonia and strontium hydroxide.

Strontium nitrate $Sr(NO_3)_2$ may be prepared by dissolving the carbonate in dilute nitric acid. On allowing the hot concentrated solution to evaporate, the anhydrous nitrate separates out in transparent crystals belonging to the regular system, generally in octahedrons modified by faces of the cube. Its sp.gr., according to Schröder, is 2·96. It possesses a cooling taste, and when thrown upon red-hot charcoal deflagrates, burning with a red flame. Owing to the fact that this salt lends itself most readily to the production of red fire, it is much used in pyrotechny.

On cooling a dilute solution of strontium nitrate a hydrate $Sr(NO_3)_2,4H_2O$ separates out in large monoclinic prisms, which rapidly effloresce in the air. Strontium nitrate is soluble in about twice its weight of water at 13°, and in an equal weight at 100° (Mulder). It is but slightly soluble in alcohol and almost insoluble in strong nitric acid.

Strontium phosphide Sr_3P_2 is prepared by reducing tristrontium phosphate with carbon in the electric furnace. It forms brownish-red crystals, density 2·68, and decomposes water yielding phosphoretted hydrogen and strontium hydroxide.

Di-strontium ortho-phosphate $Sr_2H_2P_2O_8$, or $SrHPO_4$, is obtained by precipitation of solutions of strontium salts with disodium phosphate as a white amorphous powder, insoluble in water but soluble in acids or ammonium salts. It is not decomposed by aqueous solutions of alkalis.

After being heated strongly to the fusing-point it exhibits phosphorescence.

According to Kühn, a mixture of di-strontium and mono-strontium phosphates is formed when the strontium salt is incompletely precipitated in the cold by the alkaline phosphate.

Potassium strontium phosphate $KSrPO_4$, and sodium strontium phosphate $NaSrPO_4$, are obtained by ignition of one molecule strontium pyrophosphate with a molecule of potassium or sodium carbonate and extraction with water. They are, however, somewhat readily decomposed by water, the residue being invariably found to contain neutral strontium phosphate. According to Joly (Compt. rend. 104, 905) a molecule of HNa_2PO_4 reacts with one of $SrCl_2$ in three stages. A gelatinous trimetallic phosphate is first formed, which then becomes crystalline, and is afterwards transformed into di-strontium phosphate, the solution becoming acid. The temperature remains stationary at first, while cubic crystals of $NaSrPO_4,9H_2O$ begin to form, almost insoluble in cold water. If the precipitate is allowed to remain in the liquid and phenolphthalein added, and then sodium hydroxide, a white gelatinous precipitate, rapidly crystallising, is formed. When the indicator changes, one equivalent of alkali has been added, and the whole of the strontium is precipitated as $NaSrPO_4,9H_2O$.

Strontium pyrophosphate $Sr_2P_2O_7$ is obtained by precipitation as an amorphous powder, rapidly becoming crystalline when the liquid is kept warm. It is insoluble in acetic but soluble in stronger acids. Heated to 100° the hydrate $Sr_2P_2O_7,H_2O$ is left, but above that temperature the water is driven off.

On adding strontium nitrate to a boiling solution of sodium pyrophosphate, a precipitate forms which is probably a mixture of strontium pyrophosphate with a double salt.

Di-strontium arsenate $SrHAsO_4$. When a solution of HNa_2AsO_4 is added to one of $SrCl_2$ a precipitate of $SrNaAsO_4,H_2O$ is thrown down; when the filtrate from this is evaporated, a white precipitate of the di-strontium salt is obtained (Salkowski). According to Joly (Compt. rend. 104, 905), when 1 molecule $SrCl_2$ solution is added to one of HNa_2AsO_4 no precipitate is formed, the solution remaining alkaline; but after some time, if the sides of the vessel are rubbed, a crystalline precipitate separates, and the liquid becomes acid. In 24 hours large cubic crystals of $NaSrAsO_4,9H_2O$ (isomorphous with corresponding phosphate) are deposited. On addition of one equivalent NaOH the precipitation is complete.

Strontium silicate. According to Kirwan, equal weights of strontia and silica fuse, with formation of an amber-coloured glass and a black and white enamel. Vauquelin found that with 3 parts of strontia a solid grey mass is formed, difficultly soluble in water, but readily in dilute acids. According to Kuhlmann, strontium carbonate, digested in solution of silica is converted into a hydrated strontium silicate.

Strontium monosulphide SrS is prepared by reduction of the sulphate with coal or other form of carbon. It is a white, granular, semi-fused and brittle mass. It is decomposed by treatment with a large quantity of boiling water, with formation of strontium hydroxide, which crystallises out on cooling, and strontium sulphydrate, which remains in solution:

$$2SrS+2H_2O=Sr(OH)_2+Sr(SH)_2.$$

If a less quantity of water be employed, nearly pure hydrosulphide is extracted, while the residue on treatment with more water gives a solution of almost pure hydroxide.

The strontium sulphide obtained by heating 100 parts $SrCO_3$, 30 parts sulphur, and 5 parts arsenious oxide shows a greenish-blue phosphorescence if the carbonate has been prepared from the chloride and ammonium carbonate, but a greenish-yellow if precipitated by sodium carbonate (Verneuil, Compt. rend. 103, 600). According to Becquerel (*ibid.* 104, 551) the colour of the phosphorescence varies with the temperature. At −20° it is violet-blue, at +40° pale blue, at 90° a greenish-yellow, and at 150° orange. The reverse series of colour-changes is noticed as the temperature falls.

Strontium tetrasulphide SrS_4. When the monosulphide and sulphur are digested in water in the proportion of 1 to 3 molecules, and the solution allowed to evaporate below 17°, a brown syrup is obtained which crystallises at 8° to a mass of the composition $SrS_4,6H_2O$. This substance is very hygroscopic, and soluble in alcohol as well as in water. On exposing the solutions to the air, strontium thiosulphate remains in solution, sulphur and a little $SrCO_3$ being deposited. On heating the syrup to 100°, or concentrating under the air-pump between 20° and 25°, a light-yellow solid of the composition $SrS_4,2H_2O$ separates. Heated above 100°, its own water of crystallisation decomposes it. It is insoluble in carbon disulphide.

When an alcoholic solution of SrS_4 is exposed to air, transparent ruby-red rhombic crystals are formed of the composition $SrO{\cdot}SrS_4,12H_2O$, which are decomposed by water. They are probably identical with Gay-Lussac's disulphide, which he obtained by allowing a solution of strontium sulphide to stand.

Strontium pentasulphide SrS_5 is obtained when the monosulphide is digested in water with 4 molecules of sulphur, but is only known in solution. On attempting to isolate by evaporation under the air-pump, a mixture of the tetrasulphide and sulphur is obtained (Schöne, Pogg. Ann. 117, 56).

Strontium hydrosulphide $Sr(SH)_2$ is readily obtained by saturating strontia water with sulphuretted hydrogen, or by passing sulphuretted hydrogen through water holding strontium sulphide in suspension. Also by dissolving the monosulphide in a small quantity of boiling water, by which it is decomposed into soluble sulphydrate and insoluble hydroxide. By evaporating the solution obtained by the first method, Berzelius obtained the hydrosulphide in large striated prisms, which on heating melt in their water of crystallisation, then give it off, together with sulphuretted hydrogen, and leave a residue of the monosulphide.

Strontium sulphite $SrSO_3$. Strontia commences to absorb sulphur dioxide at 230° with production of $SrSO_3$. Strontium sulphite is obtained by double decomposition as a white powder soluble in aqueous sulphurous acid, from which solution the sulphite is again deposited in crystalline grains. The crystals are flat, rectangular tables, which are gradually converted into sulphate on exposure to air.

Strontium sulphate $SrSO_4$ is found native as celestine in large rhombic crystals and fibrous masses. The name celestine was originally given to the mineral on account of the light-blue tint which it generally possesses. By fusing potassium sulphate with excess of strontium chloride Manross obtained well-developed artificial crystals of celestine. Sulphuric acid added to the solution of any strontium salt gives a precipitate of sulphate more or less crystalline. According to Haushofer (J. M. 1887, 1, Ref. 15), solutions containing 0·1 grm. $SrCl_2$ in 20–80 c.c. water treated with 1 c.c. concentrated hydrochloric acid, give with dilute sulphuric acid very perfect rhombic crystals. Precipitated strontium sulphate has a sp.gr. of 3·7, and fuses on being strongly heated. It is less soluble in hot than in cold water, but is more soluble in acids. According to Fresenius, 1 litre of water dissolves 0·145 grm. at ordinary temperature and 0·104 grm. at 100°. This aqueous solution at once gives a turbidity with solutions of barium salts. Strontium sulphate dissolves to a considerable extent in a solution of common salt and other saline solutions, but the presence of sulphates or dilute sulphuric acid diminishes the solubility. Unlike barium sulphate, strontium sulphate is completely converted into carbonate by boiling with solutions of alkaline carbonates.

Strontium sulphate is soluble in hot, strong sulphuric acid, crystals of celestine separating out on cooling. If it is heated with strong sulphuric acid to 100° and the solution digested with an excess of salt at a still higher temperature, the acid salt $SrH_2(SO_4)_2$ separates as a crystalline powder, which changes on exposure to moist air to the hydrated salt $SrH_2(SO_4)_2,H_2O$, forming shining tabular crystals. According to Varenne and Pauleau (Compt. rend. 93, 1016) 1 grm. of $SrSO_4$ precipitated from the chloride dissolves in 1256 grms. sulphuric acid.

Strontium chromate $SrCrO_4$ is formed as a lemon-yellow precipitate, composed of slender microscopic needles, when a strong solution of chloride or nitrate of strontium is mixed with one of neutral potassium chromate. After drying over sulphuric acid or at 100° the salt is anhydrous, and remains unaltered on heating. One part of the salt is soluble in 840 parts of water at 16°. It is readily soluble in hydrochloric, nitric, and chromic acids. It dissolves with difficulty in acetic acid, and is insoluble in alcohol. No precipitate is formed in presence of acetic acid if the solution contains for 1 molecule K_2CrO_4 1 molecule $Sr(NO_3)_2$ or $Sr(C_2H_3O_2)_2$ and 30 molecules water, or for 1 molecule $SrCl_2$, 25 molecules H_2O. The separation from barium by means of K_2CrO_4 is, therefore, not complete, some $SrCrO_4$ coming down along with the $BaCrO_4$ (Meschtchersky, J. Russ. Phys. Chem. Soc. 1882, 219).

Bourgeois (J. M. 1880, 1, Ref. 351) prepared $SrCrO_4$ by heating 2 molecules $SrCl_2$ with 1 molecule K_2CrO_4 and 1 molecule Na_2CO_3 to bright redness. The $SrCrO_4$ thus obtained forms beautiful yellow rhombic lamellæ, cleaving parallel to faces of a rhombic prism, and sparingly soluble in water.

Strontium dichromate $SrCr_2O_8,H_2O$ has been obtained by Preis and Rayman (Ber. 13, 340) by dissolving $SrCrO_4$ in concentrated chromic acid and drying the product at 100°. It consists of readily-soluble dark-red crystals. A second salt, containing $3H_2O$, was obtained in the form of red deliquescent crystals.

Detection and estimation of strontium. Strontium salts colour the flame a characteristic crimson. Examined by the spectroscope, the spectrum is found to consist of a large number of bright lines, of which the orange line $Sr\alpha$, the red lines $Sr\beta$ and $Sr\gamma$, and the blue line $Sr\delta$ are most characteristic. Even in presence of a large quantity of barium salts this reaction affords a ready means of distinguishing strontium.

In its reactions strontium very much resembles barium. It chiefly differs in forming more soluble salts. Thus the sulphate, chromate, and silico-fluoride are considerably more soluble. Hence dilute solutions are only precipitated after some time by sulphuric acid or soluble sulphates, and a solution of strontium sulphate gives an immediate precipitate with soluble barium salts.

The chromate is very much more soluble, a precipitate of stellar aggregates of needles only forming with strong solutions and in absence of much acetic acid. Strontium sulphate is formed after a time if the solution is dilute, but immediately if strong, on addition of a solution of calcium sulphate to one of a soluble strontium salt, and thus strontium may be distinguished from calcium.

Strontium may be estimated as carbonate by precipitation with ammonium carbonate and ammonia from a hot solution; the carbonate is not decomposed by ignition over an ordinary Bunsen burner. It may also be estimated as sulphate, the completion of the precipitation being effected by addition of alcohol. This method, of course, can only be used when the original strontium salt is soluble in alcohol.

Atomic weight of strontium. Richards, using the bromide, obtained as mean 87·616; $O=16$. Thorpe and Francis (Proc. Roy. Soc. 83 A. 277), using various methods, obtained as mean 87·649.

G. S. B.

STROPHANTHUS. *Kombé Arrow-poison.* The seed of *Strophanthus hispidus* (De Cand.) is used by the natives of Central Africa for the preparation of arrow-poison. A paste is made by crushing the seed with water, and with this the arrow-heads are smeared. Arrows tipped in this way appear to be used both in warfare and in the chase. In the latter case the animal falls quickly, when the flesh immediately around the wound is cut away and the remainder eaten without any injurious effect. Strophanthus arrow-poison is very widely used throughout the whole of Central Africa, specimens having been obtained and sent to Europe from time to time from nearly all parts of the east and west coasts. The plant is a woody climber of the natural order *Apocynaceæ*, which ascends the highest trees and hangs in festoons from one to another. The pods contain one to two hundred seeds, each seed weighing about half-a-grain, and having attached to it a beautiful comose appendage on an extremely brittle stalk. The seed was first examined by T. R. Fraser, of Edinburgh, in 1872, who drew attention to its important physiological action on the movements of the heart, and pointed out that both its physiological and toxic action depends upon the presence of an active constituent to which he gave the name 'strophanthin' (Pharm. J. [iii.] 3, 523; 19, 660).

There has been some doubt as to the precise botanical origin of the seed of commerce. That examined by Fraser came from the East coast, has a fawn colour, and when viewed in certain positions a greenish-grey appearance. West African seed is dark-brown in colour and smaller. The latter is without doubt derived from *S. hispidus*, and to distinguish the former, which alone is recognised by the Pharmacopœia, it is described as the product of *S. hispidus*, variety *Kombé* (Oliver) (Holmes, Pharm. J. [iii.] 21, 233; Brit. Pharm. Additions, 1890, 29). *V.* also Holmes (*ibid.* [iii.] 16, 778; 17, 903); Maisch (*ibid.* [iii.] 17, 972); Hanausek (*ibid.* [3] 17, 972); Blondel (J. Pharm. Chim. [v.] 17, 249, 297, 554); Christy (Pharm. J. [iii.] 20, 318).

In 1877 Hardy and Gallois isolated an active crystalline compound from strophanthus seed which was named 'strophantin,' and which had neither the characters of a glucoside nor those of an alkaloid. Fraser, however, finds the active constituent to be a glucoside, which readily breaks up under the influence of dilute acids into an easily-crystallisable neutral compound and a sugar. The glucoside is *strophanthin*, and the neutral compound produced by its decomposition *strophanthidin*, the latter probably identical with the 'strophantin' of Hardy and Gallois. Both these compounds are toxic and bitter, and have similar physiological action. The seed also contains a large proportion of *fixed oil*, and an acid forming an insoluble lead salt, *kombic acid*, and the alkaloids choline and trigonelline have been shown to be present in small amounts (Thoms, Ber. 31, 404).

A specimen of seed examined by Fraser lost at 100° 6·7 p.c. of water, and the residue yielded successively to light petroleum 31·8 p.c. of oil; to ether, 0·8 p.c. chiefly resin and chlorophyll; to rectified spirit, 8·9 p.c. of bitter extract; and to water, 9·3 p.c. mostly mucilage and albumen. When burnt, there remained 3·5 p.c. of ash; insoluble undetermined constituents, 38·9 p.c. *Strophanthin* is found in the alcoholic extract. To obtain it a concentrated solution of the extract in water is prepared, and precipitated by a solution of tannin. The precipitate is well washed and mixed with enough moist oxide of lead to combine with the quantity of tannin employed. This mixture is allowed to digest at a low temperature for several days, and when dry is extracted successively with rectified and proof spirit. If any tannin remains in the solution, the lead oxide process has to be repeated. Excess of lead is removed from the alcoholic solutions by a stream of carbon dioxide passed for 2 or 3 days. The solutions are then evaporated to dryness, the residue exhausted with rectified spirit, and the alcoholic solution precipitated by the addition of ether. The more or less crystalline precipitate of crude strophanthin thus obtained is purified by solution in alcohol and evaporation in a vacuum. The yield of strophanthin amounts to 65 p.c. of the alcoholic extract.

A second method is to extract the seeds, which have previously been freed from fat and oil, with cold 70 p.c. alcohol. The alcohol is removed by distillation and the residue extracted with water. Lead acetate is added to the aqueous extract as long as a precipitate is produced, and then ammonium sulphate in just sufficient quantity to precipitate the excess of lead which is removed. On further addition of a large excess of ammonium sulphate the strophanthin separates in a pasty mass, and may be purified by repeated precipitation by the addition of ether to the alcoholic solution (Thoms, Ber. 31, 271).

Strophanthin is usually obtained as an amorphous mass, although crystals can be produced. Its empirical formula is not known with certainty, but analysis gives figures agreeing approximately with $C_{16}H_{26}O_8$. It readily absorbs moisture, and is capable of forming several hydrates. After drying over sulphuric acid it melts with decomposition at 170° (Feist, Ber. 31, 534; 33, 2063, 2069). It is very soluble in water or aqueous alcohol; is less soluble in alcohol, acetone, or amyl alcohol; and is insoluble in ether, chloroform, light petroleum, and carbon disulphide. Mineral acids give characteristic colour-reactions with strophanthin. Sulphuric acid in the cold gives a bright-green colour, which on heating to 43°–49° changes to olive, dark-brown, violet, violet-blue, and finally to a violet-black. A 10 p.c. solution of sulphuric acid produces similar changes of colour. Nitric acid gives colour-reactions. Hydrochloric acid dissolves it, forming a pale-yellow solution, changing to brownish-yellow. A 10 p.c. solution of hydrochloric acid forms a colourless solution, which when heated to 46°–54° for 20 mins. changes to green and dark-blue, the latter colour remaining for several hours (Fraser). If a trace of strophanthin, dissolved in a drop of water, be mixed with ferric chloride and a drop of sulphuric acid added, a reddish-brown precipitate forms, which either at once or after standing some hours changes to emerald green (Helbing, J. Soc. Chem. Ind. 1891, 575).

On hydrolysis strophanthin yields strophanthidin and a carbohydrate. Strophanthidin has the composition $C_{27}H_{38}O_7,\frac{1}{2}H_2O$. It melts at 169°–170°, but when anhydrous at 235° The sugar, *methylstrophanthobioside*

$$C_{12}H_{21}O_9OMe,$$

obtained by the hydrolysis of strophanthin, forms a colourless crystalline powder melting at 207°. When hydrolysed it yields methyl alcohol, *d*-mannose, and *d*-rhamnose (Feist, *l.c.*, and Ber. 33, 2091; *cf.* Karstein, Chem. Zentr. 1902, ii. 1514).

Kombic acid has not been isolated in a definite condition. The *oil* extracted by light petroleum does not appear, when properly washed, to possess any physiological activity. It varies in colour from pale yellow to green and brown, and in sp.gr. from 0·975 to 0·927 (Fraser), and consists mainly of the glycerides of malic and palmitic acids (Mjoen, Arch. Pharm. 234, 283). *See* also Elborne (Pharm. J. [iii.] 17, 743; 18, 219); Helbing (*ibid.* [iii.] 17, 747, 924); Gerrard (*ibid.* [iii.] 17, 923); Merck (*ibid.* [iii.] 18, 72); Adrian a. Bardet (*ibid.* [iii.] 18, 539); Castillon (J. Pharm. Chim. [v.] 17, 334); Fischer (Pharm. Post. 20, 489).

The arrow-poison of the Somalis 'ouabaïo,' the botanical origin of which is not known with certainty, contains a compound, *ouabain*, which is nearly related to strophanthin or strophanthidin. This compound is now prepared from a variety of strophanthus seeds, known in the market by the unscientific name of 'strophanthus glabrus' (Holmes, Pharm. J. [iii.] 21, 234; Arnaud, Compt. rend. 106, 1011; 107, 1162; 126, 1208, 1280; Cathelineau, J. Pharm. Chim. [v.] 20, 436). *V.* Oubaïo, vol. iv. 26. A. S.

STROPHANTOBIOSE *v.* Carbohydrates.

STRYCHNINE *v.* Vegeto-alkaloids.

STYPHNIC ACID *v.* Phenol and its homologues.

STYRACINE, *cinnamyl cinnamate* $C_6H_5{\cdot}CH:CH{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH:CH{\cdot}C_6H_5$, occurs in storax. It crystallises in needles, m.p. 14°. On saponification it forms a salt of cinnamic acid and styrone (*v.* Balsams).

STYRACOL *v.* Synthetic drugs.

STYRENE, *styrolene, cinnamene, phenylethylene* $C_6H_5{\cdot}CH:CH_2$, occurs in liquid storax (*v.* Balsams), from which it may be obtained on distillation. It is formed by reducing phenylacetylene with zinc-dust and acetic acid (Aronstein and Hollemann, Ber. 1889, 22, 1184); by heating cinnamic acid with barium hydroxide (Gerhardt and Cahours, Annalen, 1841, 38, 96): by acting upon cinnamyl alcohol with sodium amalgam (Hatton and Hodgkinson, Chem. Soc. Trans. 1881, 39, 319); by heating dragon-blood resin either alone or in the presence of zinc-dust (Bötsch, Monatsh. 1880, I, 610); by heating phenylethyl bromide with alcoholic potash (Thorpe, Zeitsch. Chem. 1871, 130); by the action of aluminium chloride on a mixture of benzene and ethyl bromide (Anschütz, Annalen, 1886, 235, 331); by acting upon phenylmethylcarbinol with phosphoric acid (Klages and Allendorff, Ber. 1898, 31, 1298). Styrene is, however, most conveniently prepared by acting upon cinnamic acid with hydriodic acid and then heating the product with aqueous potash (Fittig and Binder, Annalen, 1879, 195, 137).

Properties and reactions.—Colourless aromatic liquid; sp.gr. 0·925 at 0°; b.p. 146°; insoluble in water, but soluble in all proportions in alcohol and ether. On keeping it changes gradually into metastyrene; with the halogens and halogen acids it readily forms addition compounds; on reduction it yields phenylethene and on oxidation benzoic acid; by the action of nitrogen trioxide it is converted into a nitrite (Sommer, Ber. 1895, 28, 1328).

Distyrene $(C_8H_8)_2$, m.p. 124°, is obtained by the distillation of calcium cinnamate (Engler and Leist, Annalen, 1833, 6, 256) or cinnamic acid alone (Miller, *ibid.* 1877, 189, 340), and also by the distillation of truxillic acid (Liebermann, Ber. 1889, 22, 2255). A liquid distyrene is said also to exist, being obtained when styrene is heated with concentrated hydrochloric acid (Erdmann, Annalen, 1883, 216, 187).

Metastyrene. Styrene on keeping, especially at high temperatures, changes, slowly in the dark, more quickly under the influence of light, into another polymer, which forms an amorphous glassy mass, metastyrene; on distillation it regenerates styrene.

α-**Chlorostyrene** $C_6H_5{\cdot}CCl:CH_2$ is obtained by heating styrene chloride with soda-lime (Blyth and Hofmann, Annalen, 1845, 53, 310); liquid b.p. 199°.

β-**Chlorostyrene** $C_6H_5{\cdot}CH:CHCl$ is formed when cinnamic acid is heated with sodium hypochlorite or with potassium chlorate and hydrochloric acid (Stenhouse, Annalen, 1845, 55, 1; 1846, 57, 79); also by heating phenylchlorlactic acid with water to 200° (Glaser, *ibid.* 1870, 154, 166); also by the action of zinc-dust on trichlomethylphenyl carbinol (Jocitsch, Chem. Zentr. 1899, i. 607).

αα'-**Dichlorostyrene** $C_6H_5{\cdot}CH:CCl_2$ is formed by the action of chloral on benzene in the presence of aluminium chloride (Biltz, Annalen, 1897, 296, 259).

αβ-**Dichlorostyrene** $C_6H_5{\cdot}CCl{:}CHCl$ is formed by the action of phosphorus pentachloride on acetophenone (Dyckerhoff, Ber. 1877, 10, 120).

Trichlorostyrene $C_6H_5{\cdot}CCl:CCl_2$ is obtained by the action of alcoholic potash on phenyltetrachlorethylene (Bilz, Annalen, 1897, 296, 270).

Bromostyrenes are obtained by similar methods (Glaser, *ibid.* 1870, 154, 168; Fittig, *ibid.* 1879, 195, 142; Fincke, *ibid.* 1883, 216, 290; Jocitsch, Chem. Zentr. 1899, [i.] 607; Favorsky, *ibid.* 1899, [i.] 778; Nef, Annalen, 1899, 308, 273).

Iodostyrenes (*v.* Peratoni, Gazz. Chim. ital. 22, [ii.] 69; Liebermann and Sachse, Ber. 1891, 24, 4155).

o-**Nitrostyrene** (m.p. 12°) from β*o*-nitrophenylpropionic acid and alkalis (Einhorn, Ber. 1883, 16, 2213).

m-**Nitrostyrene** (m.p. −5°) similarly obtained (Prausnitz, *ibid.* 1884, 17, 597).

p-**Nitrostyrene** (m.p. 29°) similarly obtained (Basler, Ber. 1883, 16, 3005).

α-**Nitrostyrene** (m.p. 58°) from styrene and nitric acid (Simon, Annalen, 1839, 31, 269); by heating benzaldehyde with nitromethane and zinc chloride (Priebs, *ibid.* 1884, 225, 321); by heating phenyl*iso*crotonic acid with fuming nitric acid (Erdmann, Ber. 1891, 24, 2773).

For other *nitrostyrenes, see* Priebs, Annalen, 1888, 245, 343; Friedländer and Mahly, *ibid.* 1885, 229, 224; Friedländer and Lazarus, *ibid.* 1885, 229, 233; Lipp, Ber. 1884, 17, 1070.

STYROGALLOL (*o-Dihydroxyanthracoumarin*) $C_{16}H_8O_5$ is prepared by heating 10 parts of cinnamic acid with 17 of gallic acid and 150 of sulphuric acid for 2–3 hours at 45°–55°. The yellowish-red mass, after cooling, is poured into a large excess of water, the pale green microscopic crystals so formed are filtered off and washed with boiling, slightly acidified water, and recrystallised from alcohol, glacial acetic acid, or aniline (D. R. P. 40375; Frdl. 1877–87, 569; Jacobson and Julius, Ber. 1887, 20, 2588; Kostanecki, *ibid.* 3137).

Styrogallol forms light yellow needles which do not melt at 350° and sublime at 360° almost without decomposition. It is sparingly soluble in alcohol, acetic acid or aniline, and almost insoluble in other solvents. It dissolves in alkalis with a green colour, which on warming becomes blue, violet, and finally red. It dissolves in strong sulphuric acid with a yellowish-red colour, and when oxidised with nitric acid it yields much phthalic acid.

Styrogallol is a dyestuff which gives on mordanted materials similar shades to nitroalizarin.

With acetic anhydride it yields a *di-* and a *tri-acetyl* derivative, and when the former is digested with boiling alcohol and potassium acetate for about 2 hours, it yields a crystalline purple-coloured *potassium salt* $C_{16}H_7O_5K$ (Perkin and Wilson, Chem. Soc. Trans. 1903, 139), which readily dissolves in water with a red colour. With fuming sulphuric acid styrogallol forms a *sulphonate*. When *p*-coumaric acid is condensed with gallic acid it forms *hydroxystyrogallol* or 2 : 3 : 6-trihydroxyanthracoumarin $C_{16}H_8O_6$, which resembles styrogallol, but the presence of an additional hydroxy group causes it to be less soluble and more intensely coloured. *Triacetoxystyrogallol* $C_{16}H_5O_6(OAc)_3$ melts at 250° in a vacuum (Slama, Chem. Zentr. 1899, ii. 967).

STYRONE, *cinnamyl alcohol*

$$C_6H_5{\cdot}CH : CH{\cdot}CH_2OH$$

occurs in storax. It crystallises in thin needles; m.p. 33°; b.p. 250°; it has a characteristic smell of hyacinths. On mild oxidation it yields cinnamaldehyde; with more vigorous oxidising agents cinnamic acid.

SUBCUTIN *v.* SYNTHETIC DRUGS.

SUBERIC ACID (Ger. *Korksaüre*)

$$CO_2H[CH_2]_6CO_2H.$$

Obtained by the oxidation of the following substances with nitric acid: cork (Markownikow, Ber. 1893, 3089; Étaix, Ann. Chim. Phys. [vii.] 9, 384); castor oil (Markownikow, Étaix, *l.c.*; Tilley, Annalen, 39, 166); oleic acid (Laurent, *ibid.* 28, 258; Bromeis, *ibid.* 35, 96); stearic acid (Bromeis, *ibid.* 35, 89); linseed oil (Sacc, *ibid.* 51, 226); cocoa-nut oil (Wirz, *ibid.* 104, 271); almond oil, spermaceti (Arppe, *ibid.* 120, 292; 124, 89); palmitic acid (Schröder, *ibid.* 143, 33); paraffin (Pouchet, J. 1874, 358); by treating pyrollidine with cyanogen bromide and phosphorus pentachloride (Braun, Chem. Zentr. 1909, ii. 1993); by treating the copper derivative of dipropargyl with iodine, followed by carbon dioxide and reducing the $\Delta^{\beta\epsilon}$-hexadiinene-$\alpha\zeta$-dicarboxylic acid thus formed with hydrogen and platinum black (Lespieau and Vavon, Compt. rend. 148, 1322; 149, 997); by the oxidation of azelaone with potassium permanganate (Derlon, Ber. 1898, 1962). It has been synthesised from trimethylene bromide, magnesium and carbon dioxide (Zelinsky and Gutt, *ibid.* 1907, 3049), and by the electrolysis of an aqueous solution of the potassium salt of the monoethyl ester of glutaric acid and subsequent hydrolysis of the diethyl ester thus formed (Brown and Walker, Annalen, 261, 119). To separate suberic acid from azelaic acid, which is also produced in many of the above reactions, use is made of the different solubilities of their magnesium salts (Gantter and Hell, Ber. 1881, 1552; Derlon, *ibid.* 31, 1959).

It crystallises in white scales, m.p. 139·5° (Massol, Bull. Soc. chim. [iii.] 17, 746); sparingly soluble in water and ether, insoluble in chloroform. By heating suberic acid with chalk, suberone (*cyclo*heptanone), carbon dioxide, water and a trace of benzene are formed (Markownikow, Ber. 1893, Ref. 813). The *anhydride* obtained by heating suberic acid with acetyl chloride, melts at 62°–63° (Anderlini, Gazz. chim. ital. 24, i, 474). The *amide* melts at 208°. Twenty-six isomerides of suberic acid have been prepared.

SUBERONE *v.* KETONES.

SUBLAMIN *v.* SYNTHETIC DRUGS.

SUBLIMATION. The passage of a stable substance, when heated, into the state of vapour may take place in one of three ways:—

1. The substance is liquid under ordinary conditions; it boils at a definite temperature, depending on the pressure.
2. The substance is solid; when heated it melts at a definite temperature, and when more strongly heated it boils like an ordinary liquid.
3. The substance is solid; when heated it does not melt, but passes directly from the solid state to that of vapour at a definite temperature depending on the pressure.

Similarly in the condensation of vapour we may have (1) liquefaction; (2) liquefaction and subsequent solidification; (3) direct passage from the gaseous to the solid state.

The term *distillation* is applied to vaporisation and subsequent condensation of the first kind, *sublimation* to the corresponding changes of the third order.

Vaporisation and condensation of the second kind should be included under the term *distillation*, since it is really liquid which is converted into vapour, and which, as a rule, is first formed in the process of condensation. The term sublimation is, however, not unfrequently employed in the case of substances whose melting-points are high or are not far removed from their boiling-points, and, indeed, if the application of the term were strictly limited to changes of the third class it would not be very frequently employed in practical chemistry.

As a matter of fact, the majority of substances may undergo either distillation or sublimation, according to the pressure under which the vaporisation and condensation take place. This may be best understood by means of the diagram (Fig. 1), in which temperatures are measured as ordinates and pressures as abscissæ.

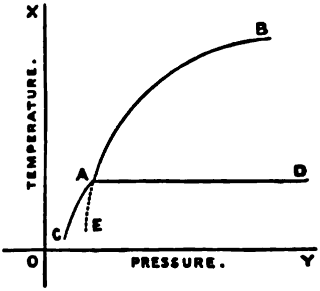


FIG. 1.

The curve AB represents the boiling-points of a substance, the curve CA its subliming-points, and the curve AD its melting-points under varying pressures. The boiling and subliming-points vary greatly with alteration of pressure, the melting-points to so slight an extent that the curve AD, drawn to true scale for any substance, could not be distinguished in such a diagram from a straight horizontal line.

All three curves intersect each other at A, called the *triple point*. The temperature at A, measured vertically from the horizontal axis OY, gives the melting-point of the substance under the pressure represented by the horizontal distance of A from the vertical axis OX; it is practically the same as the melting-point under atmospheric pressure—generally a small fraction of a degree lower.

If a solid substance is heated under pressures greater than the *triple-point pressure*, its temperature will rise until the melting-point is reached; then, after fusion, the temperature will again rise until the liquid reaches its boiling-point. The melting- and boiling-points under any given pressure are indicated by the intersection of a vertical line representing that pressure with the curves AD and AB.

If, however, the pressure is lower than the triple-point pressure, the substance cannot, under ordinary circumstances, exist in the liquid state at all, and when heated it sublimes without previous fusion at a temperature given by the intersection of the vertical line of constant pressure with the curve CA. (It is, however, possible to cool a liquid below its freezing-point without solidification taking place, and it may, indeed, be made to boil below its freezing-point. This is indicated by the dotted line AE, which is simply a continuation of the curve BA.)

The pressure at the triple point varies very greatly for different substances, but in the vast majority of cases it is far below the atmospheric pressure. Hence under ordinary conditions true sublimation rarely takes place.

The following table gives the melting-points, the boiling-points under normal pressure, and the triple-point pressures of a few substances; complete data have been obtained in only a limited number of cases:—

Substance	Melting-point—degs.	Boiling-point—degs.	Triple-point pressure
Water	0·0	100·0	4·6 mm.
Acetic acid	16·4	118·5	9·45 „
Benzene	5·6	80·2	35·9 „
Bromine	−7·1	58·7	44·5 „
Nitrogen	−214	−193·1	60·0 „
Iodine	114·3	184·3	91·0 „
Camphor	180·0	204·0	380·0 „
Mercuric chloride	288·0	303·0	554·0 „
Carbon hexachloride	188 (about)	188 (about)	1 atm.
Arsenious oxide	200 (about)	?	a little above 1 atm.
Aluminium chloride	180–185	?	a little above 1 atm.
Arsenic	500 (about)	450 (about)	above 1 atm.
Carbon dioxide	−57 (about)	−78·2	about 5·3 atm.

Some other compounds—such as mercurous chloride and indium trichloride—sublime without fusion, but exact data are wanting.

It will be seen from the table that the triple-point pressure of carbon dioxide is over five atmospheres, hence when the liquid is allowed to escape from a steel cylinder in which it has been stored under pressure, that which escapes vaporisation at once solidifies and cannot be melted in an open vessel, but passes directly into the gaseous state.

Arsenic and arsenious oxide also sublime when heated under atmospheric pressure, and carbon hexachloride sublimes if the pressure is very slightly lowered, but melts and distils if the pressure is slightly raised. Water again cannot exist as a stable liquid under a pressure lower than 4·6 mm. Below this pressure, ice, when heated, sublimes without melting.

The curve CA represents not only the subliming-points of a solid substance under varying pressures, but also the vapour pressures of the substance at varying temperatures (Ramsay and Young, Trans. Roy. Soc. 1884, i. 37), just as the curve AB represents both the boiling-points and the vapour pressures of the substance in the liquid state; hence the relation of the subliming-point of a solid to the pressure may be defined in precisely the same way as that of the boiling-point of a liquid.

The ordinary definition of the 'boiling-point' (a liquid boils when its vapour pressure is equal to the superincumbent atmospheric pressure) is, however, to some extent misleading. There is, in the first place, perhaps some ambiguity about the terms 'boiling-point' and a 'boiling' liquid. It is true that when a liquid is described as boiling, the impression conveyed is that the liquid is in a state of ebullition, but the 'boiling-point' is certainly not the temperature of ebullition. What is called the 'boiling-point' of a liquid is usually determined by placing a thermometer in the vapour over the liquid, care being taken that the thermometer bulb is always moistened by condensed liquid. It is, in fact, the condensing-point of the vapour that is directly measured.

On the other hand, in order that a bubble of vapour may form below the liquid, not only has the pressure of vapour or air over the liquid to be overcome, but also that of the column of liquid over the point where the bubble forms, and, lastly, the adhesion of the liquid to the solid surface (or possibly the cohesion of the liquid itself). In the case of a very clean smooth vessel, and a liquid very free from dissolved air, this last factor becomes very important, and the ebullition-point may be considerably higher than the 'boiling-point.' Under the most favourable conditions it is somewhat higher (Regnault, 'Relation des Expériences,' 1847, 525–529).

The boiling-point of a liquid is, in fact, not its ebullition-point—which does not depend solely on the pressure—but it is *the highest temperature attainable by the liquid under a given pressure when evaporating with a perfectly* *free surface, and when heat is received from outwards towards the surface.* It is only under these conditions, where ebullition is obviously impossible, that the boiling-point can be accurately determined by measuring the temperature of the liquid itself (Ramsay and Young, Chem. Soc. Trans. 47, 42).

In the case of sublimation this difficulty does not occur, for anything analogous to ebullition is impossible, and since the solid can only be in partial contact with the vessel containing it there is practically always a free surface for evaporation.

The ordinary definition of the 'boiling-point' of a liquid takes also no account of the fact that a law analogous to Dalton's law of partial pressures holds good for distillation and sublimation.

That this is the case is proved by the behaviour of two non-miscible liquids when distilled together (*v.* DISTILLATION). It is found that the boiling-point and the composition of the mixed vapour are independent of the relative quantities of the two liquids present, and that the 'boiling-point' is the same as that of either liquid when distilled alone under a pressure equal to its partial pressure in the mixed vapour. Hence, as the pressure of the vapour of the one liquid is without influence on the 'boiling-point' of the other, it might be inferred that the pressure of an indifferent gas, such as the air, would be without influence on the 'boiling-point' of a liquid or on the subliming-point of a solid. This is, in fact, the case, and it is really not the pressure of the atmospheric air, but that of the vapour itself in contact with the liquid or solid, that influences the 'boiling-' or subliming-point.

In ordinary cases of distillation or sublimation the vapour of the substance completely expels the air from the flask or retort; hence the substance is surrounded by its own vapour at the same pressure as that of the external atmosphere, and the 'boiling-' or subliming-point does depend—though indirectly—on the atmospheric pressure.

But if the substance be made to vaporise in the open air, or in such a manner that the rapid diffusion of the vapour prevents the complete expulsion of the air from the immediate neighbourhood of the substance, then the 'boiling-' or subliming-point does not depend on the atmospheric pressure.

Thus water, when distilled in the ordinary way under a pressure of 15 mm., boils at about 18°, but Schrötter observed in 1853 (Annalen, 88, 188) that when some water was placed on a shallow clock glass, supported by a short tripod on a second clock glass, in a bell-jar over sulphuric acid, the temperature fell to −3° when the pressure was reduced to 15 mm. More rapid diffusion and removal of vapour was effected by suspending in the bell-jar a thermometer the bulb of which was covered with a sponge soaked in water; in this case, under a pressure of 40 mm., at which the 'boiling-point' of water under ordinary conditions is 34°, the temperature fell to −10°.

The following experiments afford a still more striking proof of the correctness of the statement that the 'boiling-point' does not necessarily depend on the atmospheric pressure. A copper air-bath was heated to 205° and a thermometer, the bulb of which was covered with cotton wool and moistened with boiling water, was suspended in the bath through an opening at the top. The pressure of the atmosphere was 748 mm., and the water on the cotton wool was in a strongly-heated chamber, yet the temperature, instead of remaining at nearly 100°, fell to 66°, and remained constant at this point while the water rapidly evaporated. A second experiment was carried out under the same conditions, except that steam was introduced, so as to replace the air as completely as possible by aqueous vapour. The temperature of the bath was in this case 195°, and the steam was passed into it after the temperature of the water on the thermometer bulb had fallen to 69°; the result was an immediate rise of temperature, the highest point reached being 99°. A fall of temperature to 80° was again observed on allowing some of the steam to escape.

In these cases the 'boiling-point' certainly does not depend on the pressure of the surrounding atmosphere, and in all probability the observation that the temperature of a drop of water in the spheroidal state does not reach 100° (under normal atmospheric pressure) may be explained in the same way, the vapour round the drop of water being always diluted with a certain amount of air. Again, by passing a current of air through water or any other liquid boiling in an ordinary distillation bulb, the vapour above the liquid becomes diluted, and the result is an immediate fall in temperature, both of the liquid and of the vapour, although the liquid continues to distil rapidly, and this is the case even when heated air is introduced.

Thus by bringing about admixture of air with the vapour surrounding a vaporising substance the same effect is produced as by reducing the pressure in an ordinary distillation bulb, and in this way, in certain cases, the partial pressure of the vapour may be reduced below the triple-point pressure, so that the substance which in a bulb or test-tube would melt first and then boil, will under these circumstances sublime at a temperature below the melting-point. If the bulb of a thermometer, by repeated immersion in melted camphor, be completely covered by the solid substance, and if the thermometer be then suspended in a strongly-heated air-bath through which a moderate current of air is passing, the camphor will not melt, but will sublime at a temperature lower than its melting-point, although the total pressure is far above the triple-point pressure of camphor.

The slow volatilisation of camphor, iodine, snow, and other substances is to be explained in precisely the same way, vaporisation always taking place when the partial pressure of the vapour in the surrounding air is less than the vapour pressure of the solid substance.

Again, if the vapour of a substance which is solid at the ordinary temperature condense in the narrow neck of a retort or distillation bulb, the liquid state is first as a rule assumed, and solidification afterwards takes place; but if the same vapour be allowed to diffuse into the air, or if by any means sufficient air be mixed with it before condensation occurs, it frequently happens that the solid state is at once assumed without intermediate passage through the liquid state. This direct passage from the gaseous to the solid state must, in fact, occur if by admixture with any indifferent gas the partial pressure of the heated vapour falls below the triple-point pressure before the temperature falls sufficiently for condensation to take place.

Thus on boiling sulphur in an ordinary retort, while the vapour is rising and before the air has been expelled, the formation of small quantities of flowers of sulphur is always to be observed above the vapour; but when the air has been expelled and the sulphur vapour condenses in the neck of the retort, liquid is formed. When, however, as in the formation of flowers of sulphur on the large scale, the heated vapour is passed into a large chamber containing air, direct condensation to the solid state occurs until the temperature of the chamber reaches the point at which the partial pressure of the sulphur vapour is higher than the triple-point pressure, when liquefaction takes place.

The phenomenon is still more readily observed in the case of camphor, iodine, and other substances, the triple-point pressures of which are relatively high. Thus if we heat one of these substances in a porcelain basin and hold a cold glass funnel or a glass plate over it, the substance melts and boils in the basin, but condenses as a solid on the funnel or plate. The heavy vapour collects in the basin, so that its partial pressure in the atmosphere surrounding the substance soon rises above the triple-point pressure, when fusion takes place; but before reaching the cold glass surface the hot vapour becomes so diluted with air that the partial pressure falls below the triple-point pressure, so that when condensation takes place the solid state is at once assumed. In the purification of crude anthracene by passing steam, heated to about 230°, over the melted substance, and condensing the vapour in a chamber by jets of cold water, the steam acts as an indifferent gas, and in all probability the partial pressure of the anthracene vapour is far below the triple-point pressure when condensation takes place.

So also when condensation of moisture from the atmosphere occurs at a temperature below 0°, and when the partial pressure of the aqueous vapour is necessarily lower than 4·6 mm., there must be direct passage from the gaseous to the solid state, and the light crystalline snow flakes present all the appearance of having been formed in this way.

Although the process of sublimation is in theory quite analogous to that of distillation, yet the apparatus employed for distillation is unsuited for sublimation, for the narrow condensing tubes would rapidly become blocked by the solid sublimate. In cases of true sublimation, therefore, and also in the distillation of liquids with high solidifying points—such as anthracene, camphor, iodine, &c.—the condensing tube must be wide and comparatively short, as in the Silesian subliming pots for arsenic trioxide (*v.* ARSENIC) and in the condensers employed for the manufacture of iodine (*v.* IODINE).

The condensing tube may, indeed, be replaced by a simple flat or concave cover over the subliming pot, as in the case of ammonium chloride (Fig. 2).

The ammonium chloride is heated in the pots, and condenses in the solid state on the iron covers.

(It is true that in this case the process, under ordinary conditions, is not one of simple sublimation, since the vapour does not consist of ammonium chloride, but of a mixture of ammonia and hydrogen chloride; there is really dissociation and recombination instead of vaporisation and condensation, but practically the process is the same as that of sublimation.) It has been observed, however, by H. B. Baker (Chem. Soc. Trans. 65, 615; 73, 422) that ammonia will not combine with hydrogen chloride when both gases are very carefully dried, and that dry ammonium chloride does not undergo dissociation when converted into vapour. Johnson (Zeitsch. physikal. Chem. 61, 457) has made the remarkable observation that the vapour pressures of ammonium chloride are practically the same whether the solid is carefully dried and therefore stable or imperfectly dried and subject to dissociation.

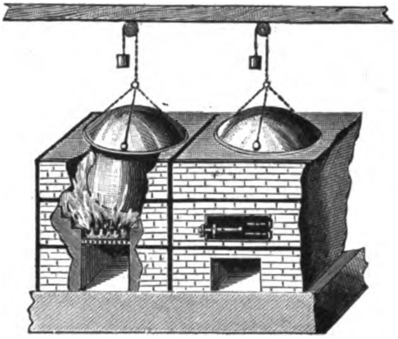


FIG. 2.

It frequently happens that when direct condensation to the solid state takes place, the substance assumes the form of a fine light crystalline powder, or of feathery flakes which are easily carried about by currents of air; hence longer flues or a succession of condensing chambers are required to prevent loss of substance. This is especially the case with such poisonous substances as arsenic or arsenic trioxide, and the condensing tubes attached to the Silesian subliming pots already referred to are supplemented by condensing chambers.

If the sublimation does not take place from a retort or pot, but from a furnace through which the hot gases pass as well as the vapour of the subliming substance, the light sublimate is very liable to be carried away, and the flues must be very long or the chambers very numerous (*v.* ARSENIC). S. Y.

SUCCINIC ACID $C_4H_6O_4$. Succinic acid and its alkyl derivatives when heated, break down into anhydrides and water. The anhydride formation takes place more readily as the hydrogen atoms of the ethylene residue of succinic acid are replaced by alkyl groups (Auwers and Meyer, Ber. 1890, 101). The alkyl succinic acids form anhydrides more readily with acetyl chloride and are more volatile in steam than their isomeric alkyl-*n*-glutaric acids (Auwers, Annalen, 285, 212) Anilic acids are produced by adding amines to the anhydride in chloroform, ether or benzene, and these on treatment with acetyl chloride or phosphorus pentachloride or by the action of heat alone yield anils.

Literature. Alkyl succinic acids, Bischoff, Ber. 1891, 1064 *et seq.*; 1890, 631; Auwers. Annalen, 285, 212; 292, 132, 152; 298, 147 *et seq.*; Bone, Chem. Soc. Proc. 1899, 5; Bone and Sprankling, Chem. Soc. Trans. 1899, 839; 1900, 654, 1298. *Dissociation Constants of Acids*, Bone and Sprankling, Chem. Soc. Proc. 1900, 184. *Arylsuccinic acids*, Avery and Upson, J. Amer. Chem. Soc. 30, 600. *Anhydrides*, Bischoff, Ber. 1890, 620, 656; Auwers and Meyer, *l.c. Anils and Anilic Acids*, Auwers, Oswald and Thorpe, Annalen, 285, 226; Auwers, *ibid.* 285, 229; 292, 132, 194; 309, 316. *Imides*, Miolati, Rea.l Accad. Lincei. 1894, i. 515; Koller, Ber. 1904, 1598. *Esters*, Bone, Sudborough and Sprankling, Chem. Soc. Trans. 1904, 534.

Succinic acid (*Bernsteinsaüre*)

$$CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H.$$

Occurs in amber (*v.* RESINS), fossil wood, and lignite (Reich, J. 1847–48, 499); in unripe grapes (Brunner and Brandenburg, Ber. 1876, 982); in various plants; in ripe wheat and barley grains (Vaudin, Ann. Agron. 1897, 23, 232); in the wood of *Goupia tomentosa* (Aubl.) (Dunstan and Henry, Chem. Soc. Trans. 1898, 228); in the juice of the sugar cane and in the calcium precipitate formed during the treatment of beet juice (Lippmann, Ber. 1891, 3299); in *Orites excelsa* (R.Br.) and other proteaceous trees as aluminium succinate (Smith, Chem. News, 88, 135); in the castor oil plant (Gram, Chem. Zentr. 1903, ii. 450); in the urine of oxen, horses, goats, and rabbits; in meat extracts (Kutscher and Steudel, Zeitsch. physiol. Chem. 38, 101; Baur and Barschall, Chem. Zentr. 1906, ii. 1351); in putrified meat (Wolff, Beitr. Chem. physiol. Path. 1903, 4, 254; Siegfried, Ber. 1895, 515). According to Helm (Arch. Pharm. 1895, 233, 191), *succinite* (ordinary amber) contains succinic acid, but *gedanite* does not. Succinic acid is formed during various processes of fermentation. The succinic acid ferment is the name given to the microbe which develops in solutions of ammonium tartrate and nutritive salts, converting them into the ammonium salts of carbonic, acetic, formic, and especially succinic acids. It is of no danger to the sugar manufacturers as their operations require a temperature of 60°, which kills it (Teixeira, Bied. Zentr. 1885, 493). In the fermentation of sugar by yeast, succinic acid is produced. It is formed not from the sugar, but by autolytic fermentation of the protein substance in the yeast cells, whereby glutamic acid is produced, and the latter is then converted into succinic acid (Kunz, J. Soc. Chem. Ind. 1907, 108; Ehrlich, Biochem. Zeitsch. 18, 391; Effront, Compt. rend. 119, 92). It is also formed by the bacteriological fermentation of asparagine (Neuberg and Cappezzuoli, Biochem. Zeitsch. 18, 424); and the schizomycetic fermentation of malic acid through *Bacillus lactis aërogenes* or of tartaric acid through *Bacterium termo* (Emmerling, Ber. 1899, 1915; König, *ibid.* 1881, 211). Succinic acid is formed by the oxidation of fats (Bouveault, Bull. Soc. chim. 19, [iii.] 562), of stearic acid (Bromeis, Annalen, 35, 90; 37, 292), Japanese wax (Sthamer, *ibid.* 43, 346), beeswax (Ronalds, *ibid.* 43, 356), spermaceti (Radcliff, *ibid.* 43, 351), sebacic and azelaic acids (Arppe, *ibid.* 95, 242; J. 1864, 377), camphor (Bredt, Ber. 1894, 2093), and of camphene (Marsh and Gardner, Chem. Soc. Trans. 1896, 84). Harries (Ber. 1904, 2708) has obtained succinic acid from rubber through fission with ozone. For methods of separating and purifying succinic acid from the commonly occurring organic acids *v.* Schoorl, Zeitsch. angew. Chem. 1900, 367.

Succinic acid is prepared by the reduction of malic or tartaric acids with hydriodic acid (Schmitt, Annalen, 114, 106; Dessaignes, *ibid.* 115, 120); of fumaric and maleic acid with sodium amalgam (Kekulé, *ibid.* Spl. 1, 133) or with colloidal platinum (Paal and Gerum, Ber. 1908, 2273); by treating ethylene cyanide with acids or alkalis (Simpson, Annalen, 118, 375); by treating the ethyl ester of β-chloropropionic acid with potassium cyanide and hydrolysing the ester thus formed (Wichelhaus, Zeitsch. Chem. 1867, 247); by heating ethylenetricarboxylic acid at 160° (Bischoff, Ber. 1880, 2162); by reducing acetylenedicarboxylic acid with sodium amalgam (Bandrowsk, *ibid.* 1879, 2212); by the hydrolysis of ethyl ethylenetricarboxylate, obtained by the action of ethylsodiomalonate on ethylchloracetate (Bischoff and Kuhlberg, *ibid.* 1890, 634); by melting gum arabic, milk sugar (Hlasiwetz and Barth, Annalen, 138, 76) or carminic acid (Hlasiwetz and Grabowski, *ibid.* 141, 340) with caustic alkali; by treating bromacetic acid with silver powder at 130° (Steiner, Ber. 1874, 184); by the electrolysis of the potassium salt of the monoethyl ester of malonic acid and subsequent hydrolysis of the diethylester thus formed (Brown and Walker, Annalen, 261, 115); by oxidising aldehydopropionic acid with nitric acid (Perkin and Sprankling, Chem. Soc. Trans. 1899, 16); by treating the semi-aldehyde of maleic acid with sodium carbonate and potassium cyanide (Fecht, Ber. 1905, 1272); by condensing sodium ethylcyanacetate with formaldehydecyanhydrin and hydrolysing the product (Higson and Thorpe, Chem. Soc. Trans. 1906, 1460); by oxidising glutamic acid with hydrogen peroxide (Daking, J. Biol. Chem. 5, 409); by oxidising furfural with Caro's acid (Cross, Bevan, and Briggs, Ber. 1900, 3132); by treating pyrrole with potassium hydroxide and hydroxylamine whereby the dioxime of succinic acid results (Zanetti, Atti. R. Accad. Lincei. 1891, i. 344).

Properties. Succinic acid crystallises in colourless monoclinic columns; melts at 182·7° (Reissert, Ber. 1890, 2244), at 185° (corr.) (Davidoff, *ibid.* 1886, 407), and boils at 261° (Krafft and Noerdlinger, *ibid.* 1889, 816), at 278·3° (corr.) (Bischoff and Kuhlberg, *ibid.* 1890, 634), and by heating strongly is converted into succinic anhydride: sp.gr. 1·554 (Tanatar and Tschelebieff, J. Russ. Phys. Chem. Soc. 1892, 22, 549), 1·562 (Marshall and Cameron, Chem. Soc. Trans. 1907, 1522). Solubility in water (Lamouroux, Compt. rend. 128, 998): 100 c.c. dissolve—

Temp.	0°	15°	20°	35°	50°	65°
Grms. acid	2·79	4·9	5·8	10·6	18·0	28·1

or, according to Marshall and Cameron (Chem.

Soc. Trans. 1907, 1522), 100 grms. of water dissolve—

Temp.	0°	20°	25°	40°
Grms. acid	2·77	6·84	8·59	14·86

At 15°, 100 parts of dry ether dissolve 1·193 parts, 96 p.c. alcohol 9·986 parts, methyl alcohol 15·73 parts and acetone 5·544 parts of succinic acid (Rau, Zeitsch. anal. Chem. 32, 483).

By heating succinic acid to a high temperature, it decomposes into carbon dioxide and water (de Coninck, Bull. Acad. Roy. Belgique, 1903, 633); heating with glycerol gives rise to acrolein and some acrylic acid (de Coninck and Raynaud, Compt. rend. 135, 1351), and fusing with caustic alkali decomposes it into oxalic and acetic acids. By the distillation of the dry calcium salt, diketohexamethylene is obtained in small quantity (Feist, Ber. 1895, 738), and also *cyclo*pentanone and furfuran (Metzner and Vorländer, *ibid.* 1897, 1885). Hanriot (Compt. rend. 101, 1156) states that by distilling the acid with excess of quicklime, ethane and carbon dioxide are obtained. By the electrolysis of a solution of the potassium salt, ethylene and carbon dioxide are the chief products (Petersen, Chem. Zentr. 1897, ii. 519). In acid solution, succinic acid is scarcely acted on by potassium permanganate (Perdrix, Bull. Soc. chim. 23, [iii.] 645); electrolytic oxidation converts it into tartaric and oxalic acids, carbon monoxide and dioxide, methane and ethylene (Clarke and Smith, J. Amer. Chem. Soc. 1899, 967), whilst hydrogen peroxide yields tartaric acid (Zinns, Mon. Scient. 16, ii. 493). Fittig and his co-workers have studied the condensations of aldehydes and sodium succinate in the presence of acetic anhydride. Acetaldehyde and its higher homologues, chloral and benzaldehyde, yield substituted paraconic acids (Annalen, 255, 18, 43, 56, 68, 96, 97, 142; Stobbe and Kloeppel, Ber. 1894, 2407), salicylaldehyde yields dicoumarin (Fittig and Politis, Annalen, 255, 275), anisaldehyde and cinnamaldehyde yield substituted *iso*crotonic acids (Fittig, *ibid.* 255, 293; 331, 151), whilst furfuraldehyde yields αγ-difurfurylidenepropionic acid and difurfurylidenesuccinic anhydride (Titherley and Spencer, Chem. Soc. Trans. 1904, 183; *v.* also Fichter and Scheuermann, Ber. 1901, 1626). Stobbe has studied the condensations which ethyl succinate undergoes with ketones in the presence of sodium methoxide. In this way γγ-disubstituted itaconic acids and γ-alkylenepyrotartaric acids are produced, the latter chiefly from ketones which contain a methylene group near the carbonyl group, and the former from ketones not containing a methylene group. Condensations have been effected with benzophenone, benzil, benzoin, cyclic ketones, &c. (Stobbe, Annalen, 308, 67 *et seq*; 314, 111; 321, 94, 105; Ber. 1895, 1122, 3192; 1899, 3354; 1904, 2232). The esters of succinic and cinnamic acids condense to form β-phenylbutane-αγδ-tricarboxylic acid (Stobbe and Fischer, Annalen, 315, 232), whilst ethylsuccinate condenses with valerolactone in the presence of sodium methoxide to form valactenesuccinic anhydride and valactenepropionic acid (Fittig, Salomon and Wernher, *ibid.* 331, 191). By heating succinic acid, acetic anhydride, anhydrous sodium acetate and zinc chloride, and distilling the residue in steam furfurane is obtained (Magnanini and Bentivoglio, Gazz. chim. ital. 24, i. 433), and on distillation of sodium succinate with phosphorus pentasulphide, thiophene is obtained. A mixture of mono- and dibromo-succinic acids is obtained by heating succinic acid, phosphorus and bromine in a sealed tube (Gorodetzky and Hell, Ber. 1888, 1730; Volhard, Annalen, 242, 141; Auwers and Imhaüser, Ber. 1891, 2233). By heating barium succinate with sodium methoxide, propionic acid is produced (Mai, *ibid.* 1889, 2136; *v.* also Kolbe, Annalen, 119, 173), and by heating the ethyl ester at 400° with alumina, tetrahydroquinone is produced (Bull. Soc. chim. [iv.] 5, 480). Ethyl succinate reacts with alkyl iodides in the presence of zinc to form γγ-dialkylbutyrolactones (Kasansky, Chem. Soc. Abstr. 1904, i. 367); with magnesium phenyl bromide to form tetraphenyltetramethylene oxide (Acree, Amer. Chem. J. 1905, 33, 180); and with hydroxylamine hydrochloride and sodium hydroxide and subsequent treatment with acetic anhydride to form succinylhydroxamic acid (Hantzsch and Urbahn, Ber. 1895, 74). Electrolysis of molecular proportions of ethyl succinate and ethyl malonate gives rise to glutaric and adipic acids (Vamzetti and Coppadoro, Atti. R. Accad. Lincei. 1903, 12, ii. 209).

Succinic acid is used as a standard in alkalimetry, acidimetry and iodimetry (Phelps, Hubbard and Weed, Amer. J. Sci. 23, 211; 24, 194; 26, 143). For this purpose the acid is prepared by the hydrolysis of the pure ester, obtained by passing alcohol vapour charged with pure hydrogen chloride into a mixture of succinic acid, alcohol and hydrogen chloride, together with the addition of a little pure fused zinc chloride, and distilling continuously at 100°–110°; *v.* also ACIDIMETRY and ALKALIMETRY. The succinates of the rare earths of the yttrium group are of importance, as it is by their fractional crystallisation that these elements are separated from each other (Lenher, J. Amer. Chem. Soc. 30, 572).

Detection and Estimation. Succinic acid does not char on the addition of sulphuric acid in the cold, but on warming darkens, sulphur dioxide being evolved. Silver nitrate gives a white precipitate in neutral solutions, soluble in ammonia; calcium chloride, a white precipitate on standing; and ferric chloride, a yellowish-brown precipitate; *v.* also Neuberg, Zeitsch. physiol. Chem. 31, 574. Succinic acid may be estimated in the presence of tartaric and lactic acids by the method of Bordas, Joulin and Raczkowski (J. Pharm. Chim. 1898, 7, 417; Chem. News, 78, 18). The solution containing the acids is exactly neutralised with N/10 potassium hydroxide, excess of silver nitrate solution is added, and the precipitate washed until the filtrate no longer gives a precipitate with potassium chromate. The precipitate, which consists of silver succinate, is washed back into the flask with water, one or two drops of potassium chromate solution added, and then sodium chloride solution is run in until the red colour disappears. The solution is then titrated back with N/10 silver nitrate solution (*v.* also Makowka, Chem. Zentr. 1908, i. 2207). ***Estimation in presence of citric and tartaric acids***, *v.* Micko, Zeitsch. anal. Chem. 31, 465. ***Estimation in plants***, *v.* Jörgensen, Chem. Zentr.

1907, i. 1224. *In wines and fermented liquids, v.* Laborde and Moreau, Ann. Inst. Pasteur, 1899, 13, 657; Kunz, Chem. Soc. Abstr. 1903, ii. 701; Muller, Bull. Soc. chim. [iii.] 15, 1203; Mestrezat, Compt. rend. 143, 185; Albaharz, *ibid.* 144, 1232; Prandi, Chem. Zentr. 1905, ii. 992; Pozzi-Escot, Compt. rend. 147, 600; Heiduschka and Quincke, Arch. Pharm. 245, 485; Blumenthal, Virchow's Archiv. 137, 539; Schmitt and Hupi, Rev. intern. falsific. 10, 199; Rau, Zeitsch. anal. Chem. 32, 482; Von der Heide and Steiner, Chem. Soc. Abstr. 1909, ii. 444.

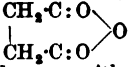
Salts. $KHC_4H_4O_4,2H_2O$; $KHC_4H_4O_4$; $KH_3(C_4H_4O_4)_2$ (Marshall and Cameron, Chem. Soc. Trans. 1907, 1514); $NaHC_4H_4O_4$; $Na_2C_4H_4O_4,6H_2O$ (Rammelsberg, J. 1855, 467; Minio, Zeit. Kryst. 31, 415);

$$CaC_4H_4O_4,H_2O;\ CaC_4H_4O_4,3H_2O$$

(Milojkovic, Monatsh. 14, 699); salts of the rare earths (Meyer, Zeitsch. anorg. Chem. 33, 31. 113; Morgan and Cahen, Pharm. J. 24, [iv.] 428; Tanatar and Kurowski, J. Russ. Phys. Chem. Soc. 39, 936); double potassium salts (Reynolds, Chem. Soc. Trans. 1898, 701). Solubilities of salts of succinic acid, *v.* Partheil, Arch. Pharm. 241, 412; Cantoni and Diotalevi, Bull. Soc. chim. [iii.] 33, 27.

Esters. The *dimethyl ester* is a crystalline solid, m.p. 19°; b.p. 195·3° (corr.); sp.gr. 1·1207 at 20°/4° (Emery, Ber. 1889, 3185). It may be prepared by the interaction of methyl bromacetate and magnesium (Spencer and Crewsdon, Chem. Soc. Trans. 1908, 1826). The *diethyl ester* is a liquid, b.p. 216·5° (corr.), sp.gr. 1·04645 at 15°/ (Perkin, *ibid.* 1884, 515). For preparation, *v. supra* (Phelps and Hubbard). *Ethylene ester,* m.p. 88°–90°; sp.gr. 1·345 at 17°/. Prepared from succinic acid and glycol or from ethylene dibromide and silver succinate (Vorländer, Annalen, 280, 177). *Aryl esters, v.* Bischoff and Hedenström, Ber. 1902, 4073 *et seq.* *Isobornyl ester, v.* Beckmann, *ibid.* 1907, 485. *Menthyl ester, v.* Hilditch, Chem. Soc. Trans. 1909, 1580. *Sanatyl esters, v.* Riedel, D. R. P. 208637; Chem. Zentr. 1909, i. 1442; Kalle and Co., D. R. P. 201639; Chem. Zentr. 1908, ii. 994.

Succinyl chloride $C_4H_4O_2Cl_2$. Prepared from succinic acid and phosphorus pentachloride (Gerhardt and Chiozza, Annalen, 87, 293; Möller, J. pr. Chem. [ii.] 22, 208); m.p. 16°–17°, b.p. 190°–192° (corr.) (Vörlander, Annalen, 280, 183; Perkin, Chem. Soc. Trans. 1888, 563). It is probably a mixture of symmetrical and asymmetrical compounds (Vorländer, Ber. 1897, 2268; Meyer and Marx, *ibid.* 1908, 2459).

Succinic anhydride  $\begin{array}{l}CH_2\cdot C:O\\ |\\ CH_2\cdot C:O\end{array}\!\!>O$. Prepared by heating the acid alone or with phosphorus pentoxide, acetyl chloride, acetic anhydride or benzoyl chloride (Gerhardt and Chiozza, Annalen, 87, 293; Blaise, Bull. Soc. chim. [iii.] 21, 643; Anschütz, Ber. 1877, 1833; Schulz, *ibid.* 1885, 2459); by treating the acid with phosphorus pentoxide in toluene solution (Bakunin, Gazz. chim. ital. 30, ii. 340); by treating sodium succinate in neutral or feebly alkaline solution with acetic anhydride (Oddo and Manuelli, *ibid.* 26, ii. 482). White solid, m.p. 119·6°; b.p. 261°; sp.gr. 1·1036 at 20°/4°: purified by recrystallisation from chloroform (Negri, *ibid.* 26, i. 77). Hydroxylamine hydrochloride reacts with the anhydride to form succinylhydroxamic acid which may be isolated by means of its barium salt (Errera, *ibid.* 25, ii. 25). Pyrogallol condenses with the anhydride to give pyrogallolsuccinin, a dyestuff giving reddish-brown shades with alumina mordants (Georgievics, Monatsh. 20, 450); hydroquinone undergoes a similar condensation (Meyer and Witte, Ber. 1908, 2457). Reduction with sodium amalgam and hydrochloric acid yields butyrolactone. Succinic anhydride condenses with *m*-aminophenols to form succinin-dyestuffs which are similar to the rhodamines (Bayer and Co., D. R. P. 51983; Frdl. ii. 86); with 1·8-naphthylenediamine it yields a dyestuff, green in acid solution (Bayer and Co., D. R. P. 202354; Chem. Zentr. 1908, ii. 1397) (*v.* TRIPHENYLMETHANE COLOURING MATTERS).

Succinic peroxide $C_4H_4O_4$ and *persuccinic acid* are formed by the action of hydrogen peroxide on the anhydride (Clove and Houghton, Amer. Chem. J. 1904, 32, 43; *v.* also Vanino and Thiele, Ber. 1896, 1724).

Succinimide. Prepared by heating succinic acid with ethylene cyanide (König, J. pr. Chem. 69, [ii.] 1; Miller, J. Amer. Chem. Soc. 16, 433); by distilling ammonium acetate (Landsberg, Annalen, 215, 173); by the interaction of succinonitrile and benzoic acid (Matthews, J. Amer. Chem. Soc. 1898, 650); by the partial hydrolysis of succinonitrile with sulphuric acid (Bogert and Eccles, *ibid.* 1902, 20); by heating acetonitrile with succinic acid (Miller, *l.c.*); by the action of ammonia on succinic anhydride (D'Arcet, Annalen, 16, 215); by distilling a mixture of succinic anhydride and carbimide (Dunlap, J. Amer. Chem. Soc. 18, 332); m.p. 125°–126°; b.p. 287°–288° (Menschutkin, Annalen, 162, 166). Phosphorus pentachloride reacts with succinimide to form tetrachloropyrrole, which is converted into pyrrole by treatment with zinc-dust and caustic potash (Ciamician and Silber, Ber. 1883, 2398). By electrolytic reduction in sulphuric acid, pyrrolidine is produced (Tafel and Stern, *ibid.* 1900, 2224; Zeitsch. physikal. Chem. 54, 443), whilst electrolysis of an aqueous solution yields succinic acid and ammonia (Pannain, Gazz. chim. ital. 35, ii. 94). Reduction with sodium amalgam and hydrochloric acid yields butyrolactone (Fichter and Herbrand, Ber. 1896, 1192); ammonia gas converts succinimide at −10° into succinamide (Roubtzoff, Chem. Soc. Abstr. 1886, 141); potassium hypobromite converts it into β-aminopropionic acid (Hoogewerff and van Dorp, Rec. trav. chim. 10, 4). Crystalline compounds with phenols (*ibid.* 1900, 19, 32); compound of silver succinimide with hexamethylenetetramine (D. R. P. 217897; Chem. Zentr. 1910, i. 701). The hydrogen atom of the imino group is capable of replacement by metals and organic radicles. For substituted alkyl succinimides *v.* Meister, Lucius and Bruning, Eng. Pats. 15327, 15328; J. Soc. Chem. Ind. 1894, 800. The metallic derivatives of succinimide are of importance as when dissolved in water and warmed, colloidal solutions of the metallic oxides are obtained in many cases. *Copper succinimide* (Tschugaeff, Ber. 1905, 2899; Ley, *ibid.* 1905, 2199; Ley and Werner, *ibid.* 1906, 2177). *Silver succinimide* (Ley and Schaeffer, *ibid.* 1906, 1259).

Nickel succinimide (Tschugaeff, *ibid.* 1906, 3190). Complex metallic derivatives (Tschugaeff, *ibid.* 1907, 1973).

Succinanil and **Succinanilide** *v.* Dunlap and Cummer, J. Amer. Chem. Soc. 25, 612.

Succinamide, m.p. 242°–243°, *v.* Henry, J. 1885, 1333.

Aminosuccinic acid *v.* ASPARAGINE.

***iso*Succinic acid.** *Methylmalonic acid*

$CH_3{\cdot}CH(CO_2H)_2$.

Prepared by treating *a*-cyanopropionic acid with potash (Wichelhaus, Zeitsch. Chem. 1867, 247); by the action of potassium cyanide on the potassium salt of *a*-bromopropionic acid (Lassar Cohn, Annalen, 251, 349) or on ethyl *a*-brompropionate (Pusch, Arch. Pharm. 232, 186; Byk, J. pr. Chem. ii. 1, 19); by the dry distillation of the esters of methyloxalacetic acid (Wislicenus and Kiesewetter, Ber. 1894, 796); by boiling silver cyanoform with water, isolating the nitrile and hydrolysing the latter with sodium hydroxide (Hantzsch and Osswald, *ibid.* 1899, 648).

Properties. Crystallises in colourless prisms, m.p. 135° (W. and K.); sp.gr. 1·455 (Tanatar and Tchelebieff, J. Russ. Phys. Chem. Soc. 22, 548); solubility in water (Massol and Lamouroux, Compt. rend. 128, 1000): 100 c.c. dissolve

Temp.	0°	25°	50°
Grms. acid	44·3	67·9	91·5

Readily soluble in alcohol, ether, and acetic acid. Electrolysis of an aqueous solution of the acid yields acetaldehyde, ethylene, carbon dioxide, carbon monoxide, oxygen and hydrogen (Petersen, Chem. Zentr. 1897, ii. 519; Zeitsch. physikal. Chem. 33, 698; *cf.* Lassar Cohn, Annalen, 251, 349). Potassium permanganate oxidises it to acetic acid, carbon dioxide and water (Perdrix, Bull. Soc. chim. iii. 23, 645); nitric acid converts it into carbon dioxide, acetic acid and trinitromethane (Franchimont, Rec. trav. chim. 5, 281). The potassium salt of the monomethylester yields on electrolysis the diethyl esters of the two symmetrical dimethylsuccinic acids (Brown and Walker, Annalen, 274, 42). Ethylsodiomethylmalonate condenses with ethyl *a*-bromobutyrate to form symmetrical methylethylsuccinic acid (Auwers, Annalen, 298, 147); with ethyl *a*-brom*iso*butyrate to form *aa*-dimethylglutaric and trimethylsuccinic acids (Auwers and Jackson, Ber. 1890, 1611; Bischoff, *ibid.* 1891, 1046; Auwers and Köbner, *ibid.* 1891, 1929); with ethyl *γ*-chlorobutyrate to form *a*-methyladipic acid and *β*-dimethylglutaric acid (Montemartini, *ibid.* 1896, 2058; Gazz. chim. ital. 26, ii. 259; *cf.* Bone and Sprankling, Chem. Soc. Trans. 1899, 849); with ethyl *β*-iodopropionate to form *a*-methylglutaric acid (Auwers and Titherley, Annalen, 292, 209); with ethyl-*a*-brom*iso*valerate in alcoholic solution to form *cis*-methyl*iso*propylsuccinic acid and in xylene solution to form a mixture of *cis*- and *trans*-methyl*iso*propylsuccinic acids (Bentley, Perkin and Thorpe, Chem. Soc. Trans. 1896, 270); with esters of unsaturated acids to form esters containing a four carbon atom ring (Michael, Ber. 1900, 3731; Svoboda, Monatsh. 1902, 842).

Dimethyl ester. Colourless liquid, b.p. 178°–179·5° (770 mm.).

Diethyl ester. Prepared from diethyl sodiomalonic ester and methyl iodide (Perkin, Chem. Soc. Trans. 1896, 1476; Michael, J. pr. Chem. ii. 72, 537); colourless liquid, b.p. 198·5°–199° at 765 mm. (corr.).

Methylmalonamide $CH_3{\cdot}CH{<}^{CONH_2}_{CONH_2}$. Prepared from malonamide, methyl iodide, sodium methoxide and methyl alcohol, or from methylmalonyl chloride and aqueous ammonia (Meyer and Bock, Annalen, 347, 104); m.p. 212° (Conrad and Schulze, Ber. 1909, 730). The *anilide* melts at 214° (Comanducci and Lobello, Chem. Soc. Abstr. 1905, i. 271; 1907, i. 409).

Amino-methylmalonic acid *v.* ASPARAGINE.

SUCCINITE *v.* AMBER.

SUCRAMINE. The ammonium salt of saccharin: known also as 'Lyons sugar.'

SUGAR (Fr. *sucre*; Ger. *Zucker*) is the generic name for a group of bodies belonging to the class of compounds known as carbohydrates, which occurs naturally in the vegetable or animal kingdom, or may, in some cases, be formed synthetically.

The sugars in general possess a more or less sweet taste, are crystallisable, are readily soluble in water, less soluble and in some cases insoluble in alcohol, and are insoluble in ether and similar solvents immiscible with water. They are optically active, *i.e.*, their solutions rotate the plane of polarised light to the right or left; whilst some precipitate cuprous oxide from Fehling's solution, an alkaline solution of cupric sodium tartrate. Another important property of some sugars is their behaviour towards phenylhydrazine, insoluble compounds being formed, a reaction which proves of much value in special cases of differentiation. Then certain of the sugars undergo alcoholic fermentation with yeast, and behave in a characteristic manner with mineral acids, both dilute and concentrated. Each individual member of the sugar group may be considered either as an aldehyde or as a ketone of hexatomic alcohols, the first being termed aldoses, and the latter ketoses. The sugars are divided into three groups: (1) Mono-saccharides, having the formula $C_6H_{12}O_6$, which may be further subdivided into bioses, trioses, hexoses, &c., according to the number of atoms of carbon they contain. This group includes dextrose (glucose, grape sugar, or starch sugar), mannose, galactose, lævulose (fructose, honey sugar, or fruit sugar), sorbose, arabinose, and xylose. (2) Di-saccharides, having the formula $C_{12}H_{22}O_{11}$ which may be considered as composed of two mono-saccharide residues, less a molecule of water. This group includes sucrose (cane sugar, saccharose, or crystallisable sugar), lactose (milk sugar), maltose and melibiose. (3) Tri-saccharides, which have the formula $C_{18}H_{32}O_{16}$, the best known member of which is raffinose (melitriose or gossypose) (*v.* CARBOHYDRATES).

Properties of sucrose, saccharose, or cane sugar.[1] The disaccharide sucrose crystallises

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[1] So as to avoid confusion in the nomenclature of this article, it may be pointed out that 'cane sugar' implies the commercial product, whether it be obtained from the sugar cane or the sugar beet. 'Sucrose' is applied to the chemically pure body, the principal constituent of the commercial product. By the term 'reducing sugars' is meant a mixture of dextrose and lævulose in unequal proportions; while 'invert sugar' implies a mixture of the same two sugars, but in equal proportions.

from its pure aqueous solution in the monoclinic system. When pure it has a sp.gr. of 1·589 at 15°. It is freely soluble in water, in direct proportion to the temperature; a saturated aqueous solution at 15·5° contains 66 p.c. of sugar and has a sp.gr. of 1·326. It is sparingly soluble in absolute alcohol, its solubility in this medium increasing with the amount of water present. On very slowly evaporating an aqueous solution of sucrose, large crystals of 'sugar candy' are produced. The rapidity of crystallisation is influenced not only by the concentration and temperature of the solution, but also by the nature and amount of the foreign substances present, reducing sugars, certain salts, and organic non-sugar bodies having an inhibitive effect.

Sucrose rotates the plane of polarised light to the right, its specific rotatory power being $[\alpha]_D^{20^\circ}66{\cdot}5$. When heated alone it melts at 160°, but in presence even of traces of water it is decomposed at temperatures above 100°, when a dark-coloured mixture of various bodies collectively termed 'caramel' results. Treatment with dilute mineral acids, or with the enzyme *invertase*, hydrolyses sucrose to a mixture of equal parts of dextrose and lævulose (invert sugar), but if concentrated mineral acids be employed decomposition occurs. Sucrose is capable of uniting with alkalis and alkaline earths, to form sucrates or saccharates, the most important of which are the calcium, barium, and strontium compounds. The mono- and di-basic calcium saccharates are soluble in water, but the tri-basic compound is insoluble. On passing carbon dioxide slowly into a fine suspension of tri-basic calcium saccharate in water, the sucrose is liberated and calcium carbonate precipitated. With salts, such as the alkali chlorides and nitrates, sucrose also forms double compounds. On mixing sucrose with an alcoholic solution of α-naphthol in presence of sulphuric acid, a characteristic colour appears, a reaction that is extremely delicate, and for this reason much used for detecting traces of sugar in very dilute solution.

Occurrence of sucrose. Sucrose is found most abundantly in the sugar beetroot (*Beta vulgaris* [Linn.]), in the sugar cane (*Saccharum officinarum* [Linn.]), in sorghum (*Sorghum vulgare* [Pers.]), in maize (*Zea Mays* [Linn.]), in the maple (*Acer saccharinum* [Wangenh]), and in certain palms (such as *Caryotaurens Nipa fructicans*, *Borassus flabellifer* [Linn.], *Cocos nucifera* [Linn.], and *Avenga saccharifera* [Labill.]). It is also present in the sap of nearly all the higher plants; but only a few of these contain it in sufficiently large amount, and in a pure enough state to permit of its profitable extraction.

Production of sugar for consumption. The sugar consumed in civilised countries is obtained, almost entirely, from (1) the sugar beetroot, and (2) the sugar cane. A small proportion of the world's production of sugar is also derived from the maple and palm trees, and from sorghum. Whereas the sugar produced from the beetroot and the sugar cane is roughly 6,600,000 and 8,600,000 tons per annum respectively, or a total of 15,200,000 tons per annum, that from the maple and palm is only 500,000 and 150,000 tons per annum, or about 3 and 1 p.c. respectively of the total beet and cane production.

(1) **The sugar beetroot**. As now grown, the sugar beetroot (*Beta vulgaris*) is a hardy biennial plant, long under cultivation in France, Germany, Austria, Russia, Holland, Belgium, Norway, Sweden, Denmark, Italy, Spain, and more recently introduced into the United States, Canada, Australia, and New Zealand.

From the original Silician white beet, the Vilmorin and the Wanzleben types have been derived, and from these a great number of varieties, differing not only in the shape of the root but also in the form and size of the leaves, have been created by the different seed growers. Of these may be mentioned Wohanka's 'W.E.R.' and 'W.Z.R.'; Dippe's 'Best'; Aderstedter's 'A,' 'B,' and 'C'; and the various Désprez, Simon-Legrand, Knauer, and Jules-Roberts varieties.

In shape a good beet is rather long and conical (see Fig. 1); it is regular and not forked, and does not throw out 'fingers and toes.' Its flesh is firm, not very soft, and gives juice only under pressure, and its colour may be white, rose, or grey. In weight the beetroot, without its leaves, may vary between 1 and 2 lbs., according to the seed and the conditions of climate and cultivation.

FIG. 1.

By means of patient cultivation and selection, the sugar content of the beetroot has been raised during the past fifty years from 10 to 18 p.c.

(2) **The sugar cane.** The sugar cane is a kind of gigantic grass. It belongs to the natural order *Gramineæ*, the tribe *Andropogoneæ*, and the genus *Saccharum*. It may be divided into the roots; the stalk, which is made up of a series of joints or internodes (see Fig. 2); and the leaf, in which under the influence of chlorophyll and sunlight the starch is elaborated, to be afterwards transformed into sugar and stored in the stalk. According to the colour, the length and girth of the stalk, and the length of the internode, a great number of varieties are differentiated. Formerly much confusion in the nomenclature of different canes had arisen, but now the classification has, to some extent, been systematised by the work of the different experiment stations and botanical

gardens. Eckert and Deerr[1] have done much towards collating the literature of the subject, and have arranged the most important varieties of the sugar cane as follows: (1) The Otaheite (which is stated to be identical with the Bourbon, Lahaina, Louzier, Keni-keni, Portii, and Cuban); (2) Cheribon canes, including the Yellow Violet, Purple Violet, the Transparent or Ribbon cane, and the Tibboo Batavee of the Straits Settlements; (3) Tanna Canes, which may be striped, white, or black; and (4) the Salangore, Cavangerie, Uba and Bamboo canes. The sugar cane is essentially a tropical plant. It thrives to the greatest perfection in a warm climate that is moist, with moderate intervals of dry heat tempered by sea breezes. Rain is very necessary, though it may be replaced to a great extent by a rational system of irrigation. The propagation of the cane is usually effected by means of cuttings from the stalks, the upper joints nearest the leaves (the so-called 'cane tops') being mostly used for this purpose. From each eye or bud, a new plant is put forth, and these gradually form roots of their own, ultimately becoming independent of the parent cutting. Previous to 1885, it was believed that the sugar cane was incapable of producing fertile seeds; but shortly after Harrison and Bovell of Barbados demonstrated, not only that the sugar cane could produce fertile seeds, but also that from these seeds new varieties possessing superior qualities, as regards high sugar content and resistance to disease and drought, can be propagated by a system of selection. As to the chemical composition of the cane, considerable differences may occur according to the variety and the conditions of the soil and climate, but the limits are fairly represented by the following figures; sucrose, 11 to 16 p.c.; reducing sugars, 0·5 to 1·5 p.c.; fibre, 8 to 15 p.c.; organic non-sugar, 0·5 to 1·0 p.c.; and ash, 0·5 to 1·0 p.c. The reducing sugars consist of dextrose and lævulose, the former sugar generally predominating. Amongst the organic non-sugars are included (*a*) nitrogenous compounds as albumins, nucleins, albumoses, peptones, amines, amino acids, and (*b*) non-nitrogenous bodies, as cellulose, fat, wax, gum, chlorophyll, &c. In addition the following organic and inorganic acids and bases are found: malic, succinic, oxalic, glycollic, acetic, sulphuric, phosphoric and silicic acids; potash, soda, lime, magnesia, alumina, iron and manganese oxides.

FIG. 2.

Raw and refined sugars. In the manufacture of sugar from the beet or cane, 'raw sugar,' which may vary in colour from dark brown to pale yellow, according to its quality, is first produced in the factory; but before being put on the market for consumption, raw sugar is generally refined in the refinery or sugar-house, which usually is an establishment separate from the factory. Sometimes, however, sugars made in the factory are consumed directly, without being refined, as in the case of high-class beet and cane sugars, so-called 'direct consumption sugars,' or in that of 'moist' sugars, such as Demerara, having a distinctive cane flavour, or of 'plantation whites.'

In this article, an account will be given of: (*a*) the manufacture of raw beet sugar; (*b*) the manufacture of raw cane sugar; and (*c*) the refining of raw beet or cane sugar.

(*a*) MANUFACTURE OF RAW SUGAR FROM THE BEET.

Briefly stated, the operations involved in the manufacture of sugar from the beetroot are as follows: (1) extraction of the juice from the beetroot; (2) clarification of the juice; (3) concentration of the juice to syrup; (4) crystallisation of the sugar from the syrup; (5) separation of the crystals; and (6) treatment of the separated syrup and the working-up of the after-products.

Extraction of the juice from the beetroot. On arriving in the neighbourhood of the factory, the roots are placed in heaps or silos, to be there stored until they can be passed into manufacture. From the place of storage, they are transported along a hydraulic carrier, provided with stone and sand catchers, to the factory building, and raised by means of a bucket elevator to the washers (Fig. 3) to be cleansed from all adhering stones and mud. After washing, the beets are lifted to an upper floor of the building, usually by a bucket elevator, to the weighing machine, which may be either an ordinary scale, or, preferably, may be of the more modern automatic type, taking about 10 cwt. in each weighing. From the hopper of the weighing machine, the beets are directed into the slicer (Fig. 4), to be there cut up into fine, long shreds, technically known as

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[1] Bulletin 26, Hawaiian Sugar Planters' Association.

'cossettes' 'slices,' or 'chips,' somewhat resembling vermicelli, in which form the extraction of the sugar is most readily effected.

In the early days of beetroot manufactured sugar, extraction of the juice was accomplished by submitting the rasped roots to hydraulic pressure, but now extraction is always carried out by means of a process of systematic lixiviation, so-called 'diffusion,' in a battery of 10 to 14 vessels termed 'diffusers' or 'cells,' arranged usually, in up-to-date factories, in a straight line, but sometimes in a circle. In shape, diffusers vary somewhat, but the general and approved type is that of a vertical cylinder, with top and bottom in the form of truncated cones (Fig. 5). Both top and bottom openings are provided with securely fitting covers, the top one being opened usually by turning to one side, while the bottom one is generally counterpoised, and provided with an hydraulic joint. At the side of each diffuser is the 'calorizator,' which re-heats the juice as it passes from one cell to another in the battery. The battery of diffusers is provided with suitable pipe connections, so that either water may be admitted to each vessel, or else the liquid contained in any vessel may be passed to its neighbour or drawn off when the operation is completed.

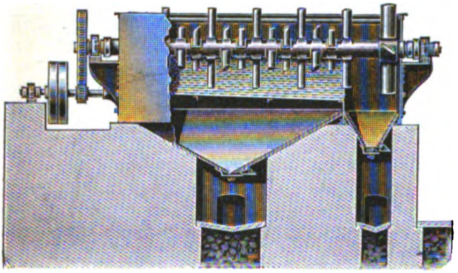
Fig. 3.

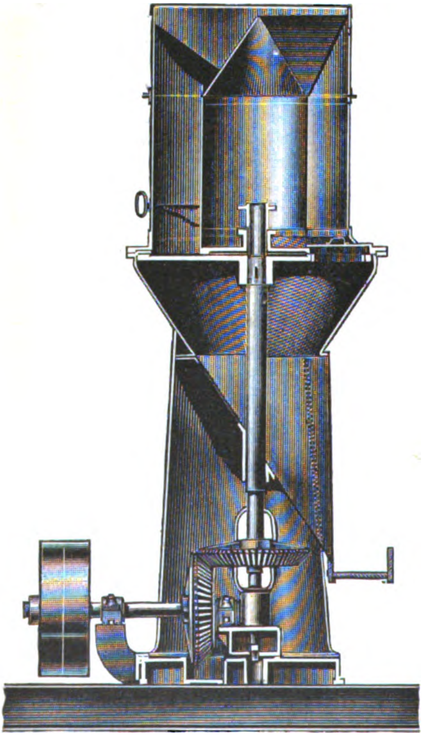
Fig. 4.

On commencing diffusion, the cossettes or slices or chips are conveyed from the slicers by a travelling band and directed by shoots into the top of the vessel to be filled, which is then securely closed. After filling the 10 or 14 diffusers with cossettes, hot water at 87°-90°C. from a tank situated at a convenient height is turned into the first diffuser, entering at the bottom, and rising up through the mass.

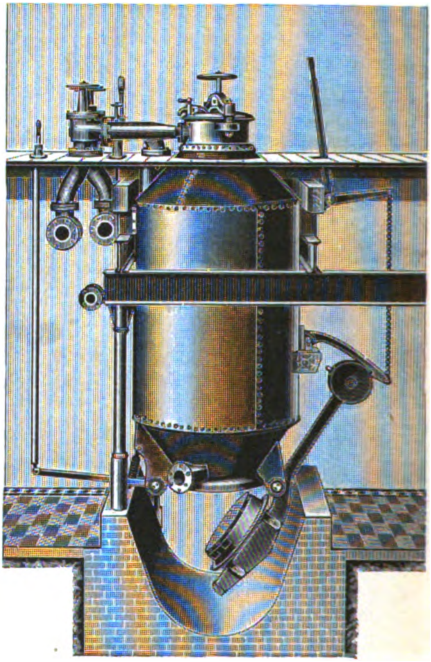
Fig. 5.

Dialysis of the soluble constituents in the cells of the cossettes, *i.e.* of sugar and certain mineral and organic non-sugar substances, now takes place through the cell-wall into the surrounding water. In cossettes there are, however, a certain number of ruptured and torn cells, usually from 6 to 7 p.c., so that during 'diffusion' the contents of these cells are simply dissolved by the water. After a few minutes, the liquid in the first diffuser, now a weak solution of sugar and non-sugar substances, is passed through the calorizator, in which it is heated, into the second vessel. From the second vessel, the liquid is sent through the calorizator into the third, and so on till it reaches a vessel, generally the sixth, in which dialysis practically ceases, the density of the juice in the cell being almost equal to that of the solution outside. After passing the sixth vessel, therefore, the solution termed 'diffusion juice' is sent to the storage tank to be ready for the next stage of manufacture, viz. clarification. Immediately the contents of the first diffuser are passed to the second, another lot of hot water at 87°–90° is run in, after which the same process is repeated, this liquid going through the several vessels, finishing, however, at the seventh instead of the sixth. This operation continues until the whole battery of diffusers is at work. After a time, the cossettes in the first diffuser are exhausted, at which stage the circuit is broken and the second diffuser becomes the first. From the diffuser out of circuit, the exhausted cossettes are discharged through the bottom opening, usually by means of compressed air. This vessel is again filled and placed in circuit, becoming the last member of the battery, the cycle of operations then going on continuously. As to the temperature to which the liquid is heated in the calorizator on passing from one diffuser to the next, and the time of treatment in the various diffusers, these vary, often considerably, in almost every factory, and depend largely on the plant and the nature of the cossettes being worked.

(2) *Clarification of the juice.* When the diffusion juice leaves the battery it is cloudy, contains some matter in suspension, and is more or less dark in colour. It has a density of 14°–17°Brix, and contains 12–15 p.c. of sugar, as well as the greater part of the soluble constituents of the beet, such as the potassium and sodium salts of phosphoric, sulphuric, hydrochloric, oxalic, and tartaric acids, proteins, pectins, &c., and a small amount of invert sugar. In reaction it is slightly acid.

In order to separate the suspended fibre, cellular tissue, and coagulated albumen, the juice is passed through a pulp-separator, which generally consists simply of a vertical cylinder containing a perforated sheet-iron basket, and from thence it goes through a juice-heater (Fig. 6). There it is heated to 75°–80°, which has the effect of coagulating a portion of the albumen present, besides preparing it for clarification.

In the beet sugar factory, clarification is always carried out in two stages: in the first, lime is added to the heated juice; and in the second the lime is removed by precipitation with carbon dioxide.

In the first stage, termed 'defecation,' or 'liming,' either dry caustic lime in powder, or else slaked lime in the form of milk at 20°Bé., may be used; and the addition is made in an ordinary tank provided with an agitator and steam coil, although it is sometimes carried out continuously in a special liming apparatus. Various views have been expressed on the relative merits of 'wet' and 'dry' defecation, but reliable investigations indicate that both yield equally satisfactory results, provided certain precautions are observed. Whichever method be used, the temperature should be at least 75°, and preferably 80°–85°, but not higher than 90°C., and the duration of contact between lime and juice should be from 5 to 10 minutes. As to the quantity of lime to be used, it may be stated that true defecation can be effected in the laboratory with only 0·5–0·75 p.c., on the weight of juice; but that this small amount is never feasible in practice, as juice thus treated can be filtered only with great difficulty. From 1·0–1·5 p.c. of lime may be used; but then it is necessary, especially when working roots that are not fresh or not fully ripe, to facilitate filtration by the addition of a little kieselguhr. In most factories, it is usual to add 2–3 p.c. of lime; and with this amount it is generally found that the juices are well defecated, light in colour, and filter readily, giving a good cake in the filter-presses.

Regarding the action of the lime on the diffusion juice, it may be pointed out that partial precipitation and partial decomposition of the non-sugar bodies occur. The free acid and acid salts present are neutralised; and insoluble salts formed with organic and inorganic acids, particularly oxalic and phosphoric acids, while potash, soda, and the organic bases present are liberated. Albumen is decomposed more or less completely, with the formation of albumoses, peptones, polypeptides, and amino acids; whilst the invert sugar is resolved into saccharic and lactic acids. In addition to its chemical effect, lime also acts mechanically, since it entrains particles and filaments of the root suspended in the juice.

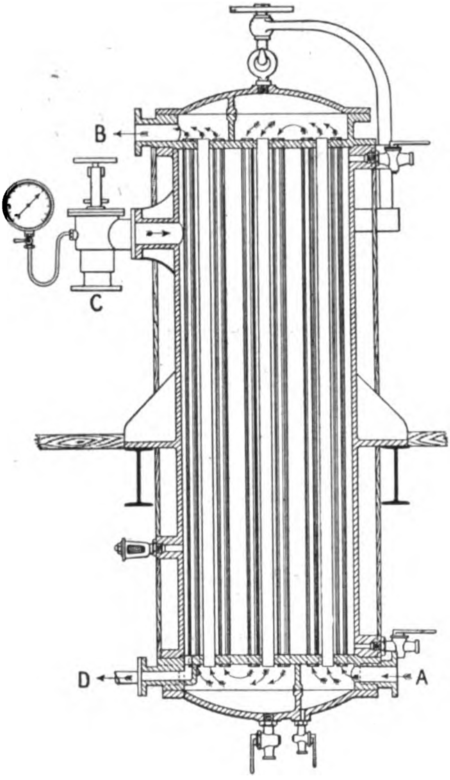

FIG. 6.

After liming, the juice is ready for the second stage of the clarifying process, namely 'carbonatation,' 'carbonation,' or 'saturation'; and for this purpose it is run into tanks, in which the treatment with carbon dioxide can be suitably effected. Carbonatation or saturation tanks may be circular or rectangular (Fig. 7), and are provided with steam coils for heating, and a special gas distributing apparatus designed to effect the best utilisation of the carbon dioxide during the operation.

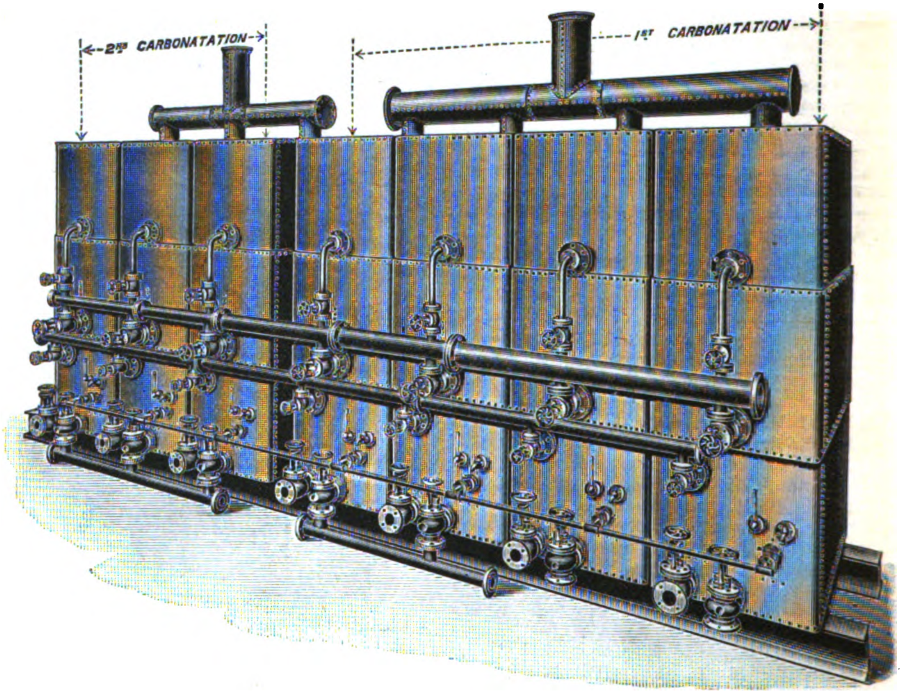

Fig. 7.

On passing the gas into the limed juice, at first there is formed a complex combination of calcium oxide, calcium sucrate, and calcium carbonate, the so-called 'sucro-carbonate of lime,' which is very gelatinous. As the operation proceeds, this body is gradually decomposed, finally with the formation of sugar and calcium carbonate. Saturation must be carefully carried out, and is continued until samples taken from time to time show that the precipitate, technically termed the 'scums,' is granular, and separates readily, leaving the supernatant liquid quite clear. Usually the gas is passed in

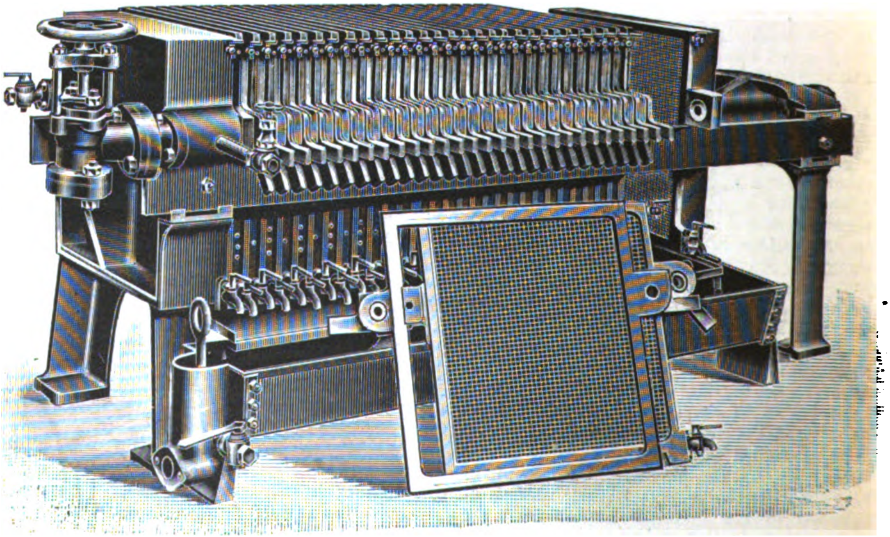

Fig. 8.

until the alkalinity on titration is about 0·1 p.c. calcium oxide, using phenolphthaleïn as indicator, but not longer, otherwise the precipitated impurities including some of the colouring bodies, commence to re-dissolve. In order to eliminate the remaining alkalinity, the 'first saturation juice,' after being passed through a filter-press (Fig. 8), must be submitted to the 'second saturation.' This is now nearly always carried out continuously, after sometimes adding a small amount of lime, about 0·5 p.c.; and generally in this operation both carbon dioxide and sulphur dioxide are used. If only carbon dioxide be used, a separate 'third saturation,' employing sulphur dioxide follows, but in any case the final alkalinity is reduced to 0·01–0·04 p.c. calcium oxide. Whether two or three saturations have been used, the juice obtained is filtered, often through presses as before, after which it is ready for evaporation to the state of syrup. It is therefore pumped up to the evaporator supply tank for this purpose.

It may here be pointed out that the saturation treatment has a slight effect in purifying the juice otherwise than by removing the lime added during defecation, since a small amount of mineral and organic matter is thrown down. As to the exact *rôle* of sulphur dioxide, continental authorities differ, but it is generally agreed that the juices are slightly decolorised, that lime salts unacted upon by the carbon dioxide are precipitated, that juice thus treated subsequently crystallises better owing to decreased viscosity, and finally that the sugar obtained keeps better on storage.

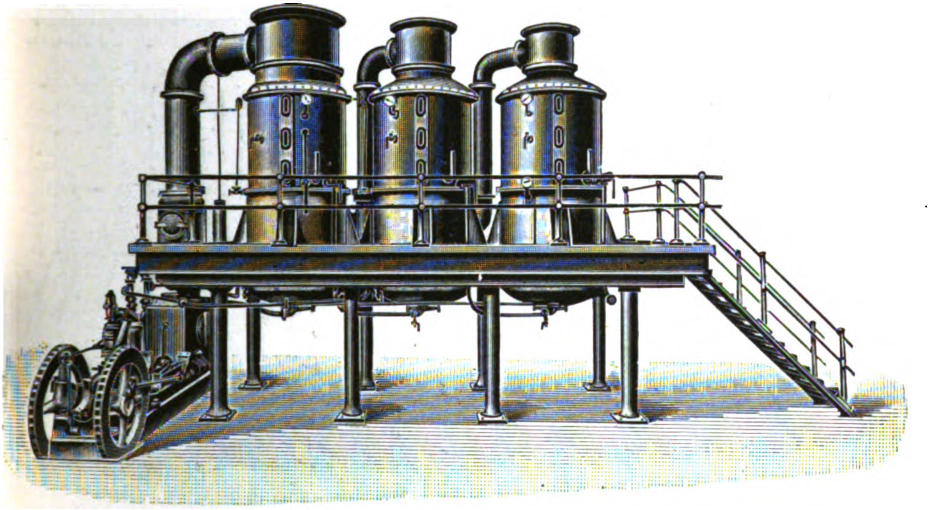

FIG. 9.

(3) *Concentration of the juice.* If the process of clarification has been well conducted, the juice should now be of a fine amber colour. Usually this 'thin-juice' has a density of 12°–13°Brix. It is next concentrated to a 'thick-juice' or syrup of 55°–60°Brix, about 80 p.c. of its water thus being removed.

This is done in one or other of the large number of multiple effect evaporators, which vary greatly in construction, and may be classified as follows: (1) the vertical, submerged tube type, the so-called 'Standard' system (Fig. 9), such as the Stillman, the Hagemann, or the Chapman evaporators; (2) the horizontal submerged tube type, such as the original Rillieux, and the Wellner-Jelinek evaporators; and (3) those of the film type, such as the Yaryan, the Lillie, and the Kestner (Fig. 10) evaporators.

It is now general to supply the first vessel of the multiple effect with exhaust steam. For heating purposes in other parts of the factory, such as the vacuum pans, the different juice and syrup heaters, or the calorizators of the diffusion battery, it is usual to take the necessary steam from one of the vessels of the triple or quadruple effect. Such an arrangement of utilising vapour is termed an 'extra steam' system.

In beetroot factories, in which the necessary amount of exhaust steam is not available for supplying the evaporators owing to centralisation of the motive power, and in which high pressure steam must consequently be used for other heating purposes, it is now becoming general to use a 'pre-evaporator' of the Pauly-Greiner or other type. This apparatus receives steam at a pressure of about 30 lbs., and in it the juice is partly concentrated, giving off vapour at about 15 lbs., which is used for the vacuum pans, juice-heaters, &c. Although in this way the juice may be heated to 115°–120°, it has been fully established that no decomposition of sucrose takes place, provided that the juice be kept sufficiently alkaline. By the use of such an apparatus, the heating surfaces of pans, heaters, &c., may be made proportionately small.

As the juice concentrates, certain salts are thrown out of solution, and are mostly deposited on the heating surfaces. Such an incrustation or scale conducts heat very badly, and greatly diminishes the efficiency of the evaporato Numerous mechanical devices have be proposed for preventing or diminishing scale formation during evaporation; but these are not widely used, so that it is necessary during the Sunday intermission to resort to chemical cleaning by boiling out with dilute sodium hydroxide or carbonate, followed by hydrochloric acid, after which the residue may generally be readily removed by means of brushes and scrapers. Pellet has made a special study of the scale of the effect of the beet sugar factory,[1] indicating the varying composition according to the particular vessel.

While evaporation is proceeding, a small amount of the juice may be 'entrained' or carried over with the vapour, sugar thus being lost. This may be prevented by the use of suitable baffles, or one or other of the patent forms of preventers, or again by a larger vapour space. It is, nevertheless, customary to periodically test the condensed water of the evaporators for sugar by means of a-naphthol, underlaying with a little concentrated sulphuric acid.

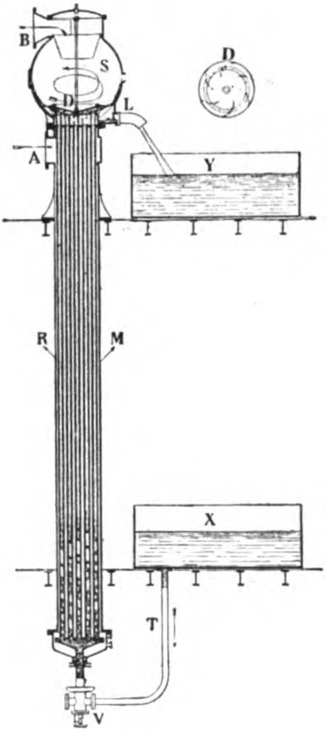

FIG. 10.

It was stated above that the alkalinity (to phenolphthaleïn) of the juice entering the evaporators is generally between 0·01 and 0·04 p.c. calcium oxide. When the juice is concentrated to 55°–60°Brix, this alkalinity should become 0·05–0·20 p.c., but it does not reach this figure, owing principally to the volatilisation of the ammonia present and the decomposition of amino acids and acid amides, and is usually reduced to about 0·02–0·03 p.c. Nevertheless, the alkalinity is generally too high to be sent directly to the next stage, viz. crystallisation in the vacuum pans; and it is customary to further reduce it to about 0·005–0·010 p.c. by first bringing the juice almost to boiling-point in a thick-juice heater, and then treating with either carbon dioxide or sulphur dioxide in some form of continuous apparatus, until the desired alkalinity is reached. Lastly, the juice is filtered through a press or sand filter.

(4) *Crystallisation of the sugar from the syrup.* As previously stated, concentration is continued in the multiple effect as far as 55°–60°Brix. Beyond this density, operations have to be very carefully conducted, and crystallisation or 'graining,' in order to be fully under control, must be conducted under reduced pressure in a single effect apparatus, otherwise known as a 'vacuum pan' (Fig. 11).

Usually vacuum pans are vertical, with a conical bottom, and are heated by coils, which may either be superimposed or else arranged in one plane on the 'lyre' system. Vacuum pans of the horizontal type are not much used now. As to size, in general, it may be said that a large pan, although it requires less attention, is not altogether advantageous, chiefly on account of the large amount of steam it takes from the evaporators on starting. In beet factories, the capacity of the pans used may vary between 20 and 50 tons.

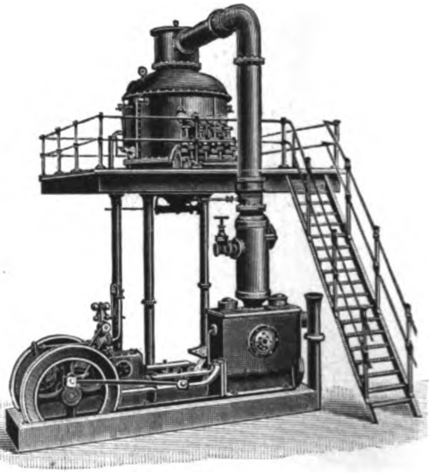

FIG. 11.

When boiling, the object of the pan-man is to form a certain amount of crystals or 'grain' in the thickened syrup, and then to allow the sugar passing out of solution during evaporation to grow on these already formed crystals, without the formation of new, small crystals, technically known as 'false grain,' which subsequently cause difficulty in the centrifugals, passing through the basket into the molasses. During the process of boiling, the pan-man is entirely guided by the appearance of the sample which he takes from the pan by the 'proof-stick' and from certain empirical tests, such as 'string proof,' 'bubble proof,' 'water proof,' 'hook proof,' &c.

Briefly described, the process of boiling down the syrup in the pan is as follows: The

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[1] D. Zuckerind. 1910, 35, 596.

air pump is started and when a sufficient vacuum has been reached, an amount of syrup, depending upon whether large or small crystals are desired, is drawn into the pan. As the syrup concentrates, crystallisation or 'graining' occurs. More syrup is then gradually drawn into the pans, either continuously or intermittently, and as concentration proceeds the sugar is deposited on the already formed crystals, so that a mixture of crystals and mother-liquor, technically known as 'massecuite,' is formed. When the pan is full, the syrup supply is shut off, and concentration is continued until the massecuite reaches a certain consistency, generally containing from 5 to 10 p.c. of water. At this point the contents of the pan, called the 'strike,' are 'struck out,' and allowed to drop into either (*a*) mixers, in which case treatment in the centrifugals is carried out directly, or (*b*) else into crystallisers, in which instance the massecuite is slowly cooled and crystallisation completed as fully as possible before centrifugalling.

The mixer is a large receiver, fitted with a stirrer, and is placed immediately over the centrifugals. It is usually of such a size as to take the entire contents of the pan. The crystallisers generally used consist of horizontal vessels, either open or closed, provided with a suitable stirring gear for imparting a gentle motion to the massecuite, and also with a steam jacket or other arrangement for heating or cooling the contents.

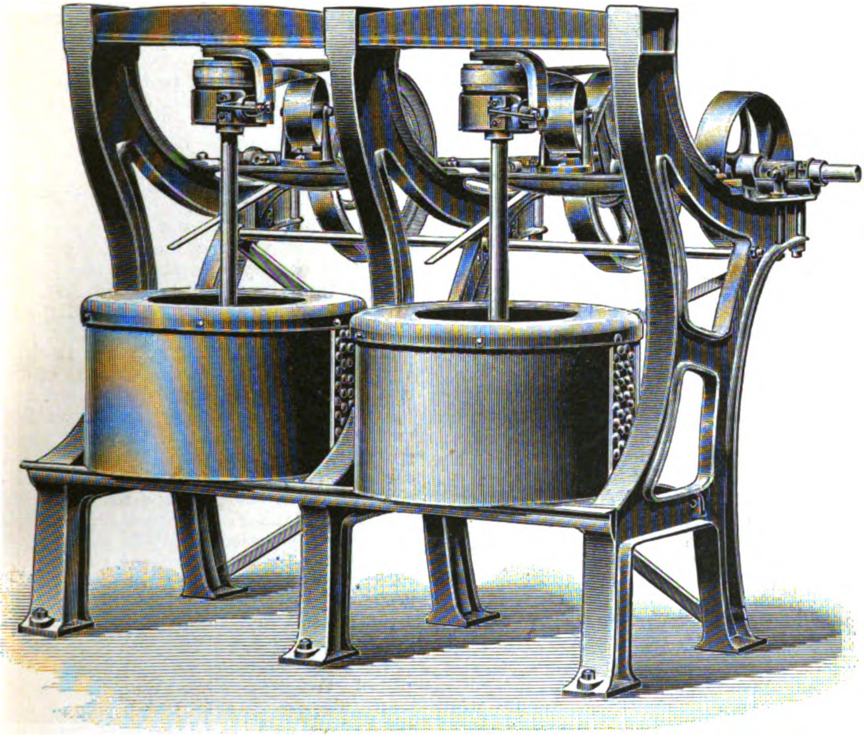

FIG. 12.

It may be mentioned that Curin (Österr.-Ungar. Zeitsch. Zuckerind. 1894, 756) has introduced an apparatus, termed a 'brasmoscope,' and Claassen (Zeitsch. Ver. deut. Zuckerind. 1897, 779) a similar instrument for enabling the workman to control the boiling and produce a uniformly good sugar.

(5) *Separation of the crystals.* It now remains to separate the crystals from the mother-liquor, or molasses, which operation, termed 'spinning' or 'machining,' is universally carried out in the beet sugar industry in a special centrifugal machine (Fig. 12).

Usually a centrifugal having a basket 40 to 50 ins. in diameter is employed. In the beet factory, both the suspended and standing types are employed, but German manufacturers still adhere largely to the latter system, although the former evidently has the greater advantages. The machine may be driven either singly or in groups, at a rate between 800 and 1500 revolutions per minute. Usually the ordinary steam power of the factory is used, electric or water-driven machines not having come into general use.

It is convenient to arrange the pans and crystallisers above the centrifugals, so that the introduction of the massecuite may be effected by gravity through a spout or gutter. If, however, this is not possible, either compressed air or a special form of pump carries the massecuite into a mixer, placed at a suitable height from which the centrifugals may be fed.

For many years past, efforts have been made to construct a continuous centrifugal, *i.e.* one into which the massecuite may be fed, and from which the machined sugar may be discharged without stopping; but none of these has given really promising results in actual working.

By 'spinning' or 'machining' the massecuite in the centrifugals, the greater part of the mother-liquor or molasses is thrown off, although a small amount always remains adhering to the crystals. The mother-liquor that is thrown off is known as 'green syrup,' or 'centrifugal syrup,' and it subsequently undergoes the procedure described under (6) *Treatment of the centrifugal syrup and working-up of the after-products.* When it is advantageous to make a raw sugar of high rendement, the amount of the adhering molasses may be reduced somewhat by a longer duration and higher rate of machining.

In making a white (unrefined) sugar for direct consumption, the syrup is removed from the crystals as completely as possible, by washing it off while still in the machines with steam, water, or concentrated sugar liquor, doing this in such a way that none, or but very little, of the crystal is dissolved. Moreover, in making white direct consumption sugar in the beet factory, a little ultramarine may be used in the pan, whilst a little may also be added to the water used for washing in the machines, or 'covering,' as the operation is sometimes called.

White sugar obtained in this way may be sold after sieving and drying as a cheap quality of 'granulated,' or it may be ground to a form of 'powdered sugar,' or, again, the crystals may be worked to 'pressed loaf sugar.' It should, however, be pointed out that such products are not to be regarded as equal to refined sugars, although they find a ready cheap market, especially on the Continent. They have not the brilliant whiteness of refined sugars, which can only be made by a further purifying treatment, involving the use of animal charcoal.

After machining, the sugar is discharged from the centrifugals into shaking gutters, which pass it to an elevator, which in turn sends it to the sieves, after which the finished raw sugar is sacked and stored.

As to the quality of a good raw beet sugar, this does not simply depend on the sucrose content, but also upon other factors. The sugar crystals should be well defined in shape and of uniform size and colour. Of more importance than the colour of the syrup adhering to the crystal is the colour of the crystal itself. If not white, a pale yellow is to be preferred to a grey, since a grey sugar is generally difficult to refine. Further, the raw sugar should have a sufficient alkalinity to phenolphthaleïn, otherwise it does not keep well on storage.

(6) *Treatment of the centrifugal syrup and the working-up of the after-products.* The syrup spun off the massecuite in the centrifugals, the so-called 'green syrup,' has a purity value of 70°–80°,[1] and contains an appreciable amount of crystallisable sugar, which is always extracted, giving a low-grade sugar termed an 'after-product.'

It was formerly the custom, and it still is to a small extent in the smaller and older Continental factories, to boil the centrifugal syrup 'blank,' *i.e.* to concentrate it to supersaturation with little or no formation of grain and allow the separation of the sugar crystals to take place in tanks, with or without the addition of inciting crystals or 'seed.' In using this method, it is necessary to repeat the boiling operation twice in order to exhaust the syrup to the purity of true molasses, and the second boiling must stand for some months before complete crystallisation is effected. Consequently, this method is a very expensive and inconvenient one, operations having to be continued after the campaign proper has terminated, although there is no doubt that the modifications introduced by Ehrhardt and Fölsche have been of much service in improving it.

According, however, to the modern method of working, in which the centrifugal syrup is boiled to grain and afterwards allowed to crystallise out while being gradually cooled and agitated in a special apparatus, called a 'crystalliser-in-motion,' this disadvantage is satisfactorily overcome.

As a rule, the vacuum pan for graining in after-product working does not differ much from that employed in boiling the thick-juice, except that it often contains an agitating apparatus to hasten the operation, since with the viscous after-product the motion during boiling is slight. Boiling may last 12–24 hours, and the finished massecuite consists of crystals and a mother-syrup of 65°–70° purity.

Generally speaking, the crystalliser-in-motion is a cylindrical vessel, preferably jacketed, provided with a horizontal shaft carrying paddles and geared to revolve very slowly. From the pan, the massecuite is run into the crystalliser at a temperature of 85°–90°C., and gradually cooled to 25°–40°C. during 4 to 5 days, water being added from time to time in such amount that the supersaturation of the liquor is kept at the optimum for regular crystallisation (*vide* Herzfeld, Zeitsch. Ver. deut. Zuckerind. 1892, 174; and Claassen, *ibid.* 1897, 809), without the formation of 'false grain.' When crystallisation is completed, the massecuite goes to the centrifugals to be separated into sugar crystals and mother-liquor. After two such operations, the mother-liquor is 'exhausted molasses,' *i.e.* molasses from which no more sugar can be obtained by crystallisation, except after some special extra treatment. It usually has a purity value of 58°–60°, if the crystallisation has been conducted in the proper manner.

In an up-to-date after-product plant, such as the Claassen (Fig. 13), or the Bock, the boiling apparatus is so arranged that its contents fall directly into the crystalliser, the contents of which are again directed through steam-jacketed channels into the centrifugals, which are immediately below.

Brief mention may be made of modifications of the general method of treating after-products that are used to a more or less extent at the present time. In the Grossé procedure, boiling and crystallisation are both carried out in a special pan, fitted with a spiral agitator, in addition to the ordinary steam coils. According

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[1] By the 'purity,' or 'quotient of purity,' is meant the percentage of sucrose in the total solid matter $= \frac{\text{sucrose} \times 100}{\text{total solids}}$.

to the Mathis method, the syrup is boiled blank to a high Brix content, filled into a special crystalliser at 95°–100°C., and there boiled under reduced pressure, graining being induced by the introduction of high-pressure steam or air. Karlik and Czapikowski have designed a horizontal graining pan in which the heating arrangement is in the form of a cross revolving about a hollow shaft at the rate of only 1–3 revolutions per minute.

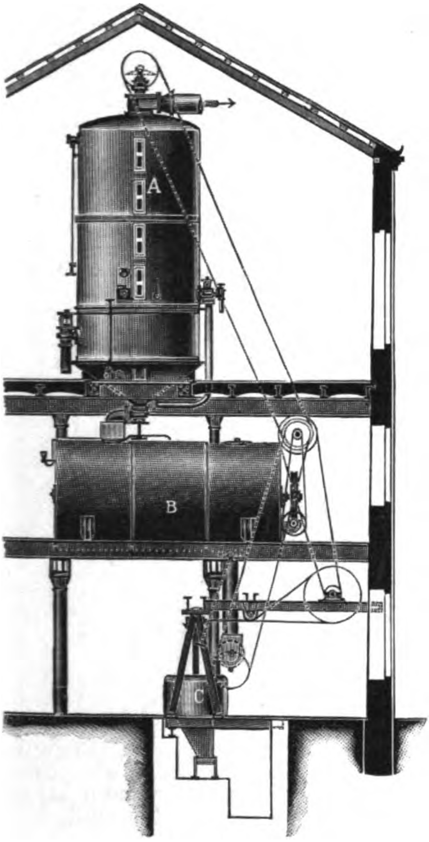


Fig. 13.

Generally the after-product obtained by one or other of the methods given above is sold directly as a low-grade sugar, but sometimes it is re-dissolved in the thin-juice, which is then worked up in the usual way. Re-solution in the thin-juice is also used in white sugar factories, *i.e.* those in which a white (unrefined) direct consumption product is made.

As to the utilisation of the 'exhausted molasses,' this may be done in several ways. On the average, the composition of the product is: sucrose, 50 p.c.; non-sugars, including mineral matter, 30 p.c.; and water, 20 p.c. From this analysis it will be observed that there is present a large amount of non-sugars, and it is these that prevent the further crystallisation of the sucrose.

In order to recover some of this sucrose, the exhausted molasses is sometimes treated by: (1) the 'osmose' process, in which, by osmosis, a syrup is obtained of higher purity; or (2) by the Steffen or Schreibler processes, or modifications of them, in which an insoluble calcium or strontium saccharate is precipitated, separated by filtration through presses, and subsequently decomposed with carbon dioxide into sugar and calcium or strontium carbonate.

Exhausted molasses, however, on the Continent especially, is now largely used for the manufacture of 'molasses cattle food,' by mixing with dried exhausted cossettes (beet pulp), dried brewers' grains, peat, alfalfa meal, or other suitable absorbent. To a large extent, also, it is sold to the distiller for the production of spirit; while a small proportion is employed in the manufacture of blacking, dyewood extracts, disinfectant solutions, &c.

(*b*) Manufacture of Raw Sugar from the Sugar Cane.

In cane sugar manufacture, the several stages are, broadly speaking, the same as those obtaining in beet sugar manufacture, but the methods used in the first two, namely, (1) the extraction and (2) the clarification of the juice, differ somewhat. In place of extraction of the juice by diffusion, milling is universally used; whilst, instead of clarification by the defeco-carbonation process, simple defecation with a small amount of lime is most generally applied. Other operations, such as (3) the concentration of the juice, (4) the crystallisation of the syrup, (5) the separation of the crystals, and (6) the working-up of the after-products, are practically the same, so that much that has been said under *Beet Sugar Manufacture* (p. 213) applies here also, and need not be repeated.

(1) *Extraction of the juice by crushing in mills.* After the cane has been cultivated, harvested, and conveyed to the factory, it is passed through mills consisting of three heavy iron or steel rollers, set with their centres at the angles of an isosceles triangle, the vertical angle of which is generally about 83°, and driven by a powerful engine through suitable massive spur and pinion gearing. In this way the cells of the cane are ruptured, and the juice containing the sugar is expressed. After falling from the rollers to the bed of the mill, the juice flows into the juice-tank, in the upper part of which is fixed a strainer to separate the grit and fine 'cush-cush,' or crushed particles of the rind and pulp of the cane. From the juice-tank, the strained juice is pumped to the clarifiers, there to be subjected to further treatment.

Formerly, the cane was simply passed through a mill consisting of only three rollers, *i.e.* it was 'dry crushed' in a 3-roller mill, and in this way it was possible to obtain an extraction of only about 60 p.c. of the sugar in the cane. According, however, to modern methods of working, in which a much higher extraction is effected, the cane is first subjected to a preparatory crushing by means of the Krajewski or similar apparatus, consisting of two rollers with pointed zigzag corrugations, and then passed through a train of 2, 3, or 4, 3-roller mills, set in tandem (Fig. 14). In addition to this, it is now customary also to treat the cane between any two mills either by (*a*) maceration, *i.e.* immersion in a bath containing dilute juice returned from the last mill; or by (*b*) imbibition, *i.e.* spraying with hot or cold water or juice. Using the Krajewski crusher, a 12-roller mill, and imbibition with 20 p.c. of water on the weight of cane, it is possible to effect as high an extraction as 90–95 p.c. of the sugar originally present in the cane. Even a higher extraction than this may be effected by using a larger amount of water; but it is not always economical to proceed so far, as with the increase of extraction the purity of the juice falls, while the extra cost of fuel for evaporation and an increased capacity of plant to deal with the greater volume of juice, must obviously also be taken into consideration. According to the different methods of milling, the extractions obtainable are as follows (British Guiana Sugar Planters' Association's Report to the West India Commission): single crushing, 76 p.c.; single crushing, with preliminary crusher, 80 p.c.; double dry crushing, 83 p.c.; double dry crushing with preliminary crusher, 85 p.c.; double crushing, with 10 p.c. imbibition, without crusher, 86 p.c.; double crushing, with 10 p.c. dilution, with crusher, 88 p.c.; treble crushing, with crusher and 20 p.c. dilution, 92 p.c.; and quadruple crushing, with crusher and 20 p.c. dilution, 94 p.c.

As to the more or less exhausted, crushed residue of cane, termed 'bagasse' or 'megass,' this is generally utilised as fuel in the sugar factory for generating the steam for evaporation, being burnt either in the wet or air-dried state, in specially constructed furnaces.

It should be pointed out that attempts were made by French and German engineers about 20 years ago to establish the diffusion process (*see* under (*a*) *Beet Sugar Manufacture*, p. 213) in the cane sugar industry. For a time it seemed probable that diffusion would become a permanent method of sugar extraction from the cane; but with the introduction of improved methods of milling, such as preliminary cutting and crushing, maceration and imbibition, the superiority of diffusion has entirely disappeared, and the process is used only in one or two places, where the economic conditions are quite exceptional. For diffusion processes in general, it is claimed (1) that they extract 96–98 p.c. of the sugar from the cane; that (2) a purer juice is obtained; and (3) that there is less danger of the stoppage of the factory from a breakdown, since if one vessel is out of order, it may be disconnected, and the work carried on with the others. On the other hand, the disadvantages are (1) that the juice is very much diluted, so that extra fuel and plant are required for evaporation; (2) that more hands are necessary; (3) there is considerable expenditure in working and maintaining the slicing plant; and (4) that the exhausted cane slices must be pressed and dried before being available for fuel.

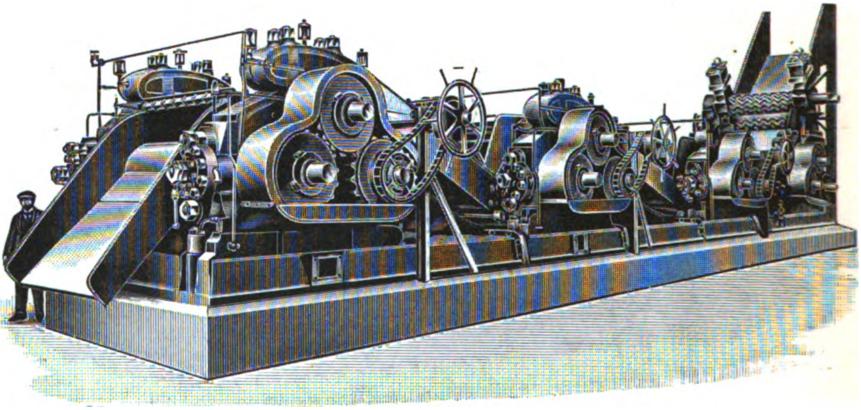


FIG. 14.

Several processes, combining milling and diffusion, have been elaborated, and of these may be mentioned the Kessler (International Sugar Journal, 1902, 4, 460), and the Geerligs-Hamaker (*ibid.* 1903, 5, 571) methods.

(2) *Clarification of the juice.* As the juice comes from the mills, it is cloudy and yellow, or dirty green in colour. In addition to sucrose, it contains as impurities gummy, protein, and colouring substances, together with mineral matter, and a more or less amount of reducing sugars, technically known as 'glucose.'

Depending upon the nature of the cane worked, the country, and the method of milling, the composition of the raw juice may vary somewhat, but generally it averages the following: sucrose, 13–18 p.c.; reducing sugars, 0·5–1·0 p.c.; gummy, protein, and colouring substances, 0·2–0·5 p.c.; mineral matter, 0·25–0·70 p.c. In now submitting it to the process of clarification, the object is to eliminate from it these non-sucrose constituents as completely as possible, so that the subsequent operation of crystallisation and separation of the crystals can be the more readily accomplished. At the present time, the two agents that are in general use in cane factories as the most economical and efficient are heat and lime, while very often either sulphurous or phosphoric acids, or both, are also employed. There are, however, considerable variations in the method of carrying out this treatment, depending upon the class of sugar, whether (*a*) refining crystals, (*b*) yellow crystals, or (*c*) white, ready consumption sugar, is being made.

(*a*) In making refining crystals, the raw juice may be passed first through a juice-heater

(Fig. 6, p. 215), in which it is raised to boiling-point, and then run into clarifying tanks (Fig. 15), where it is 'tempered' with the necessary amount of slaked lime to effect the precipitation of as much of the gummy, protein, and other impurities as possible. After settling, the clear liquor is carefully separated from the muddy deposit or 'bottoms,' and then passed on to the next stage, namely concentration. Often this method of clarification is made a continuous one, as in the Hatton system.

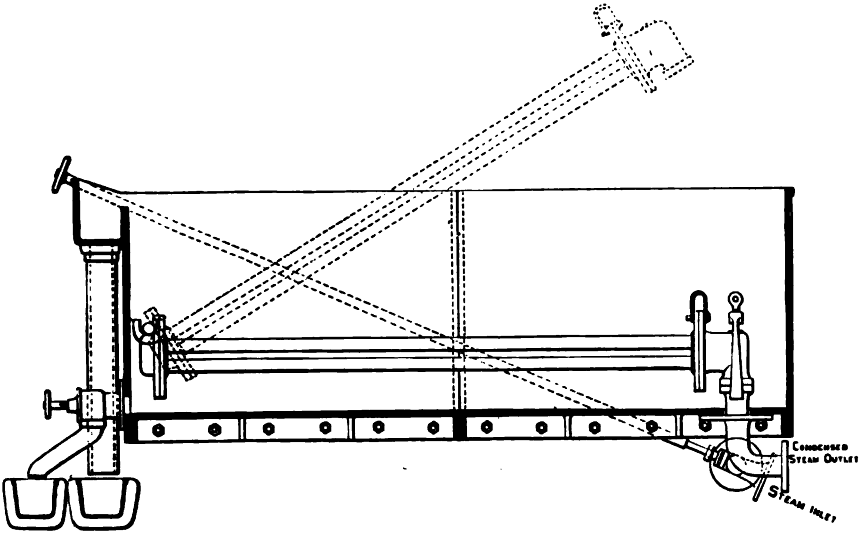


Fig. 15.

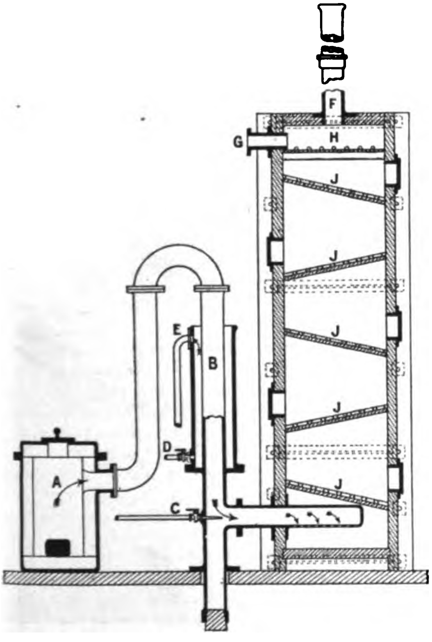


Fig. 16.

(*b*) In making yellow or Demerara crystals, it is most customary to first treat the raw juice in the cold with sulphurous acid, obtained by burning sulphur in a sulphur oven (Fig. 16). After 'sulphuring,' or 'gassing,' as it is technically termed, the juice is passed through a juice-heater (Fig. 6, p. 215) to raise it almost to boiling-point, and then run into clarifying tanks, in which it is limed, and then allowed to settle. Next the clear juice enters the eliminators (Fig. 17) or tanks provided with steam coils, where it is heated with phosphoric acid, either in the form of 'Newlanite,' or as concentrated superphosphate of lime solution, the dirty 'scums' which rise to the top surface being removed by skimming off into gutters arranged around the edge of the vessel. In this way, a pure yellow juice, free from any tinge of green, and therefore well suited for the manufacture of Demerara crystals is obtained. It is then ready for concentration. The scums and bottoms obtained in this method of treatment are boiled with lime, and clear liquor aga

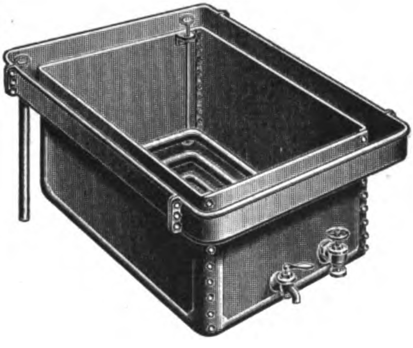


Fig. 17.

separated, either by subsidence or passing through sand-filters or filter-presses.

(*c*) In making white sugar for ready consumption, several different procedures for clarification may be followed. Until quite recently, the carbonatation process (*see* (*a*) *Beet Sugar Manufacture*, p. 215) was much in vogue; but it is now being recognised that this procedure may be replaced by a cheaper and equally efficient one, the clarification stage of which is carried out as follows (International Sugar Journal, 1911, 13, 178-179): The raw juice is mixed in the cold with 5–6 litres of milk of lime at 15°Bé. per 1000 litres, and 'sulphured' to neutrality. It is then heated to boiling-point, and run into settling tanks, the clear juice going to the evaporators, while the 'bottoms' and scums are sent through filter-presses, and the resulting clear juice also sent to the evaporators.

(3) *Concentration of the juice to syrup.* After clarification by one or other of the methods mentioned above, the juice, which may have a density of about 15°Brix, is evaporated to a syrup of about 27° to 30°Bé., or about 55 p.c. of dry substance.

In the early days of sugar manufacture, evaporation was generally effected in a series of shallow, open vessels, termed a 'copper-wall'; and, indeed, this primitive method, wasteful alike of sugar and fuel, is still used to some extent in the West Indies and on small *haciendas* in Central America and Brazil.

In the majority of cane sugar factories at the present time, however, concentration is effected *in vacuô* in some form of multiple effect apparatus (Figs. 9 and 10). What has already been said on the concentration of the juice under (*a*) *Beet Sugar Manufacture*, p. 218, applies here also, but it may be pointed out that the Pauly-Greiner pre-evaporator system of using high-pressure steam has not yet been installed in the cane sugar industry, although Deerr (International Sugar Journal, 1911, 13, 341 *et seq.*) has carried out a number of valuable researches demonstrating that this might be done with advantage.

As in the beet sugar industry, trouble is caused during evaporation by the deposition of scale on the heating tubes of the effect, the efficiency of the apparatus being thus decreased. Such scale may have a somewhat different composition to that precipitated from beet juices, and from analyses made by Pellet, the proportion of the various salts increases or diminishes according to the particular vessel of the effect, as follows:

	First vessel	Second vessel	Third vessel
Water and organic matter	29·80	26·70	18·60
Silica	0·40	23·40	69·80
Iron and alumina . .	3·80	9·98	2·80
Lime	46·30	25·80	6·80
Magnesia	1·36	0·81	1·08
Phosphoric acid . .	17·10	11·70	trace
Sulphuric acid . .	absent	absent	trace
Copper	trace	trace	trace
Undetermined . .	1·24	1·61	0·92

In cane sugar factories, the scale may also contain a more or less amount of wax, derived from the rind of the cane. In the steam chamber of the first vessel, a troublesome layer, containing oil, oxides of iron and copper, and carbon, the former coming from the steam used for heating, is sometimes observed. This deposit is best removed by treatment with petrol or benzene.

Peck (International Sugar Journal, 1911, 13, 357) has investigated the most suitable solvent for the removal of scale, containing mostly calcium sulphate, and has found that the best result is obtained with sodium carbonate followed by hydrochloric acid.

Although the greater part of the mineral and organic substances thrown out of solution during concentration deposits on the walls and tubes of the vessels of the effect, some remains in suspension in the syrup, rendering it turbid. It is of importance when making a good quality sugar to remove this impurity, since it becomes enveloped in the sugar during crystallisation, imparting a dark colour to it which cannot be removed by washing in the centrifugals.

Often, therefore, the syrup is subjected to treatment before being sent to the vacuum pans. In the case of refining crystals, the syrup may simply be allowed to stand, in order to separate the greater part of the insoluble matter. When, however, yellow crystals or white direct consumption sugars are being made, the syrup may be again 'sulphured,' or treated with phosphoric acid, then passed through sand, bag, or other suitable filters.

(4) *Crystallisation of the sugar from the syrup.* When the syrup comes from the evaporators, it has a density of about 55°Brix, and is next concentrated in the vacuum pan (Fig. 11, p. 218) to a massecuite or magma of crystals, of 92°–94°Brix.

In the cane sugar industry, owing to the demand for large pans, iron is now generally used in place of copper formerly employed; the coils are, however, made of copper or gun-metal.

In the manufacture of Demerara crystals, the fine transparent yellow colour is due largely to careful treatment during the clarification stage, and also sometimes to the addition of a minute amount of stannous chloride to the massecuite during boiling, or else to the massecuite in the centrifugals. The 'bloomer,' as it is called, produces a bright yellow colouring matter, the exact nature of which has not been determined.

When making white sugar for direct consumption, a small amount of sodium hydrosulphite ('Blankite'), or of calcium hydrosulphite ('Rédo'), about 1 part to 10,000 parts of dry sugar is often drawn into the vacuum pan a few minutes before graining. These preparations have a much more powerful reducing action than sulphur dioxide alone, and produce a marked decolorising effect on the massecuite when properly applied.

Sometimes, also, ultramarine is used in the same way, that is just at the graining point, so that each crystal may receive sufficient blue to neutralise the yellow tinge of the crystals when fully grown. As a rule, however, ultramarine is used in the centrifugals. Other colours, such as aniline blue, are now also employed for neutralising the complementary yellow of the crystal.

As in beet sugar manufacture, after boiling, the contents of the pan are 'struck out' either into mixers or else into crystallisers-in-motion, which latter may be open or closed, jacketed or unjacketed, but have a stirring gear revolving at a rate of only one revolution per minute.

(5) *Separation of the crystals.* In order to separate the crystals from the massecuite, 'machining' in centrifugals (Fig. 12, p. 219), as applied in beet sugar manufacture, is now almost always used. The primitive and wasteful method of drainage, either in a cask with a perforated bottom, or in a vacuum chest, with or without 'claying,' is now practically abandoned, even in making a low quality 'muscovado,' being only employed in the manufacture of a very crude sugar in India, parts of Central America, and elsewhere.

In the cane sugar industry, suspended and overdriven machines, with a basket 30–48 ins. in diameter, are most generally employed.

(6) *Working up the after-products.* So as to recover the sugar spun off the crystals in up-to-date cane factories crystallisers-in-motion are always used, and what has already been said about this under *Beet Sugar Manufacture*, p. 220, need not be mentioned again.

It should, however, be pointed out that some cane factories still use the obsolete method of tank crystallisation; and also that in some the old method of obtaining two, three, four, and even five crops of sugar by repeatedly boiling down the molasses, crystallising, and centrifugalling is yet in vogue.

A better scheme is to redissolve the low grade third or fourth crop sugars in the clarified juice, or else use them as 'seed' in the pan, thus recovering them as a high grade 'first' sugar. In many factories, the molasses from the first massecuite is returned to the pan, and worked up with the syrup obtained in the ordinary way; after boiling this mixture of syrup and molasses to grain, the massecuite is submitted to crystallisation-in-motion, centrifugalled, and the resulting molasses again boiled to grain, when exhausted molasses is generally obtained. Then, again, may be mentioned the so-called 'Java process' of entirely suppressing low products, by systematically returning all molasses to the pan in amounts depending upon its purity, the only final products being a good first sugar and entirely exhausted molasses.

During the cooling of low-grade massecuites, a peculiar phenomenon, characterised by the sudden evolution of gases, and termed 'froth fermentation' is often observed. It has been conclusively shown by Tempany (International Sugar Journal, 1911, 11, 588) and others that this is not due to the action of micro-organisms, but to the spontaneous decomposition of glucinates, and other products of the decomposition of reducing sugars by lime.

As to the disposal of exhausted cane molasses, it may be used for cattle food, generally using the interior pith of the cane as absorbent ('molascuit'); for the manufacture of rum, for manure, for fuel, and to a comparatively small extent for direct consumption.

(c) SUGAR REFINING.

Raw sugar, obtained from the beet or cane by one or other of the procedures given above, is seldom consumed as such, but is first refined, the products made being generally: (*a*) loaf; (*b*) cube; (*c*) granulated; (*d*) crystal; (*e*) yellow crystals; (*f*) soft pieces; and in a comparatively small amount also (*g*) castor and icing sugars.

Refining consists of the following stages: (1) preliminary washing treatment in centrifugals; (2) melting; (3) filtration; (4) decolorisation by animal charcoal; (5) boiling to grain; and (6) separation of the crystals in centrifugals or in moulds.

Generally, raw beet sugar of the quality known as 88° and 75° nett is employed by refiners, but one or two use cane sugar alone, while all replace the beet more or less by cane when the latter is the cheaper.

(1) *Preliminary washing treatment in centrifugals.* Raw sugar, as previously pointed out, consists of crystals and adhering molasses, so that by washing off the latter the purity of the sugar is considerably raised, the process of refining thus being facilitated. In the refinery, this preliminary washing treatment, sometimes called 'affining,' is best effected by mixing the sugar with syrup, so as to render it sufficiently liquid, and running it into a centrifugal machine (Fig. 12), either of ordinary or of special construction, the speed of which is generally 800 to 900 revolutions per minute. While machining, steam, water, or sugar solution, is admitted into the interior of the basket, but discontinued when the syrup leaving is light coloured, the machine then being stopped as quickly as possible.

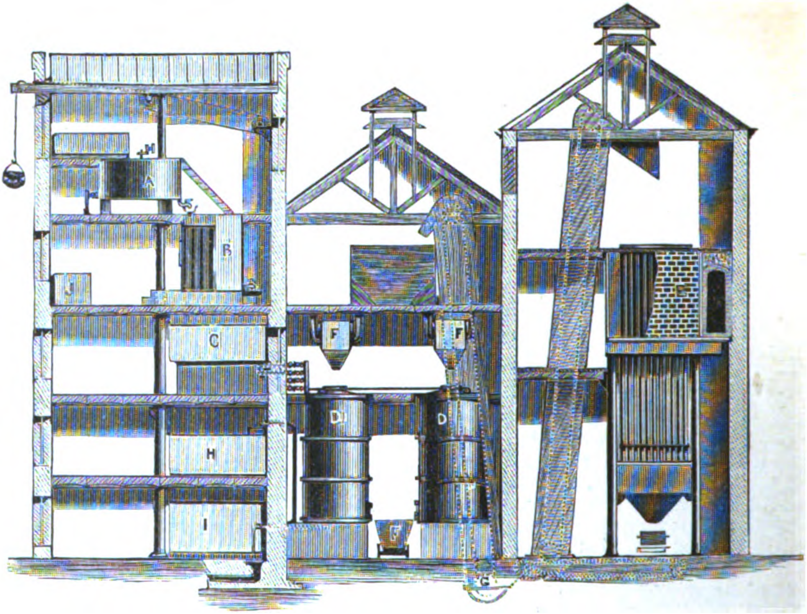
Using this process and a large-grained raw sugar, the yield of purified product may be from 80 to 90 p.c., but with low grade sugars it is usually only 65 to 70 p.c., the balance of the sugar remaining in the syrup. The treated sugar, if made from a good, 'grainy' sugar, will contain from 99 to 99·5 p.c. of sugar, but if from a raw sugar of lower quality, only 97·5 to 98·5 p.c.

As to the time required for the operation, this varies from 10 to 40 minutes, according to the quality of the raw sugar treated. With regard to steaming, the exhaust steam from the engine driving the machines will be more than sufficient. Its pressure should not exceed 5 lbs. in the pipes leading to the machines and it should be kept as dry as possible.

(2) *Melting.* After the preliminary washing treatment, the sugar is elevated to the 'blow-up' or melting pans, which are generally situated on an upper floor of the refinery (Fig. 18). These blow-ups are cylindrical in shape, and are made of cast iron. Each blow-up is capable of holding from 3 to 10 tons of sugar, and the water sufficient to dissolve the same; it is provided with a stirring gear and a copper coil, which is heated by low-pressure steam, or the coil is perforated with holes so as to blow in open steam. Thus by means of hot water and steam the sugar is rapidly dissolved, and by the addition of more sugar or water, as the case may be, the solution is brought to the required density and temperature, viz. about 28°Bé. and 160°F. Some cane sugars of low quality give a solution which is very difficult to filter, and some suitable defecant is therefore added

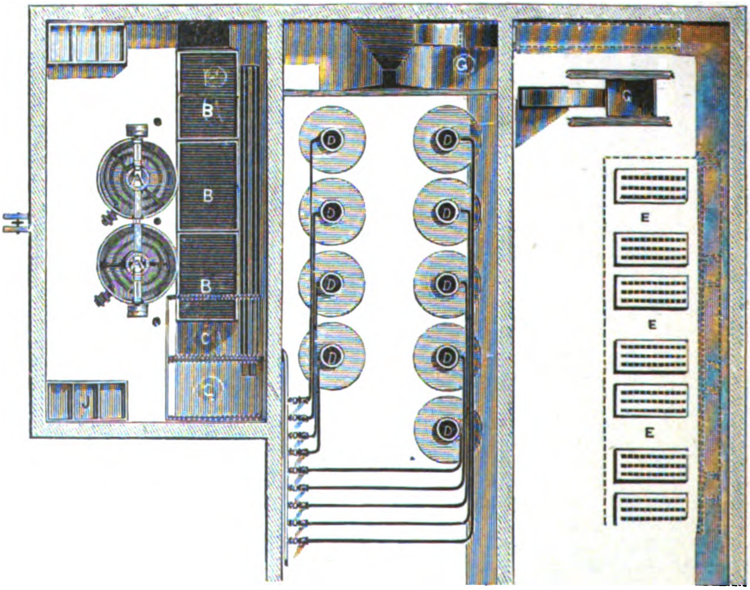
(3) *Filtration.* After the liquor leaves the blow-up it is run through a Taylor filter (Fig. 19).

The outer part of this consists of a chamber made of cast iron, of various dimensions, provided with doors. At the top of the chamber is a receiving tank from 6 ins. to 1 ft. deep, covering the entire surface, and in the bottom of this tank are a number of holes about an inch in diameter and about 9 ins. apart. Each of these holes is provided with a screw socket to receive the upper end of a bell-shaped brass nozzle which is screwed into it, and round these nozzles the



(Elevation.)

A. Blow-ups. B. Taylor filters. C. Raw sugar tanks. D. Char cisterns. E. Char kilns. F. Char trucks. G. Char elevators. H. Fine-liquor tanks. I. Sweet-water tanks. J. Washing tanks.



(Plan.)

A. Blow-ups. B. Taylor filters. C. Raw sugar tanks. D. Char cisterns. E. Char kilns. G. Char elevators. J. Washing tanks.

FIG. 18.—MELTING AND CHAR DEPARTMENTS OF A SUGAR REFINERY.

filter-bags are tied. The filter-bags are made of fine twilled cotton cloth, and are about 6 ft. long and from 18 ins. to a yard wide, and each of them is crumpled longitudinally and slipped inside a sheath made of coarse hempen cloth of an open texture. The sheath is a little longer than the filter-bag, and is from 6 ins. to 9 ins. in diameter. After the bags are inserted in the sheaths they are tied round the nozzles, which are then screwed into the sockets. . Should any one of the bags give turbid liquor the hole at the top of it should be stopped up. After the liquor has ceased to flow freely, the bags are washed repeatedly with hot water until all the 'sweet' has been extracted. This bag-water is used for melting raw sugars, steam being introduced outside the bags to keep the water hot.

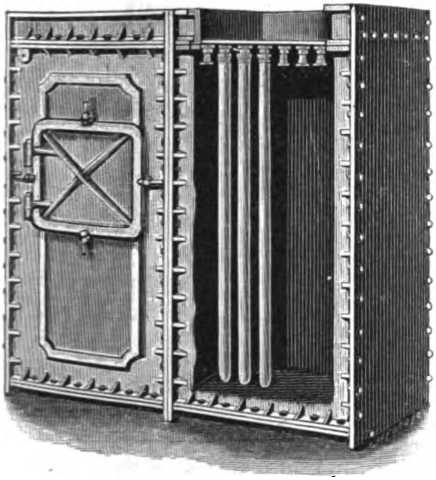


FIG. 19.

The door of the chamber is next opened, and when the filters have cooled down the nozzles are unscrewed, each bag removed from its sheath, and then turned inside out and washed several times in separate tanks. By turning the bag inside out and pushing it under water, the imprisoned air, in escaping, drives before it a good deal of the muddy impurities contained in the bag. This process is repeated several times, each time using cleaner water, and washing the dirtiest bags in the last water. In some refineries the bags are taken direct from the filters in the sweet state, and are washed in the tanks as above described, the mud being afterwards removed from the 'sweet water' by means of a filter press. A little lime is sometimes added to the muddy water to prevent fermentation and assist filtration. For most kinds of raw cane sugar it is necessary to employ Taylor filters, but beet sugar can often be satisfactorily dealt with by means of a filter-press. Various substances—including lignite, carbonised infusorial earth, brown coal, wood charcoal, animal charcoal, sawdust, &c.—have been suggested to assist the passage of liquor through the filter-press.

(4) *Decolorisation by animal charcoal.* For this purpose animal charcoal (*v.* BONE BLACK) placed in char cisterns consisting of cast- or wrought-iron cylinders, usually about 10 ft. diameter by 18 ft. high, is employed. Each cistern is provided with manholes, one at the top for introducing fresh char, and the other at one side near to the bottom for emptying out the char which has been exhausted. Each cistern has also a false bottom made of wood or iron, perforated with numerous holes and covered with scrim cloth, or blankets, so that the clear liquor coming from the char may be deprived of any char dust and may come through perfectly bright. The cisterns are filled with well-burnt char to within a short distance of the top, and the warm 'liquor,' that is, the solution of raw sugar at 28°Bé., is then allowed to flow in at the top, the cock at the bottom of the cistern having been opened to allow the air to escape. When the cistern is full, and the liquor begins to come through at the bottom, the cock is turned off, and the whole is generally left at rest for several hours, so as to 'settle.' The cock is then opened, and the decolorised liquor is allowed to flow into a tank. More raw liquor is at the same time admitted at the top of the char cistern. The speed of flow is so adjusted that the liquor may be sufficiently long in contact with the char to thoroughly utilise its power of removing the colouring and certain organic matters from solution. As long as the liquor passing through the char is colourless, it is allowed to flow into the same tank and is used for making white refined sugar. When, however, the liquor begins to assume a yellowish tinge, it is diverted into another tank, and is used for producing a lower grade of sugar. It is usual to proceed in this manner until the liquor passing away from the cistern is of a light-orange colour. The liquor is then turned off at the top, and hot water is run on to drive out the solution of sugar, but as the water mixes to some extent with the liquor a quantity of weak sugar solution is always made. This is known as 'char water,' and is employed in dissolving raw sugar, or it is sometimes, owing to its turbidity and the impurities it contains, treated separately from the liquors. It is a frequent custom to start a char cistern with good liquor, and afterwards to follow this up with lower-quality liquors. The char water, too, is often run into liquor tanks when above 18°Bé., or as long as it remains bright. When this ceases to be the case, it is run into other tanks until its density is reduced to 1° or 2°Bé., and when this point is reached it is no longer worth saving, and is therefore run down the drain. The washing of the char with boiling water is continued for some hours so as to remove, as far as possible, all organic and other impurities. The char is then allowed to drain, and is removed from the cistern to be dried and reburnt, or, as it is termed, 'revivified,' in the char kilns.

The kilns employed for this purpose may be divided into two classes, viz. revolving kilns and pipe kilns. The first consist of cast-iron cylinders, revolving in an inclined position and heated externally by fire, through which the char is passed continuously, being turned over in its passage by lifting shelves, and discharged at the lower end into an air-tight chamber. These kilns have of late been almost entirely replaced by the pipe kilns, of which various modifications are employed, one of the best being shown in Fig. 20. In this apparatus, the char is introduced through the two hoppers at the top, first into drying pipes, then into the retort pipes, where it is heated uniformly to a temperature of about 1050°F., and finally into the cooling pipes, from which it is passed into an automatic discharging apparatus, being drawn off in measured amounts at given intervals of time. After revivification, the charcoal is conveyed as required by a travelling band and elevator to a hopper placed above the char cistern.

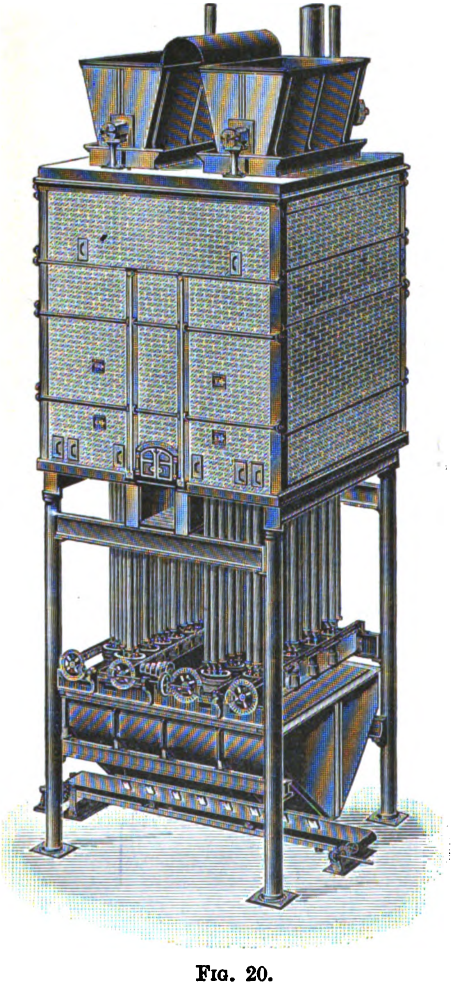


Fig. 20.

(5) *Boiling to grain.* After being sufficiently decolorised in the manner described above, the liquor is next evaporated to crystallisation point, or 'boiled to grain.' In the refinery triple or quadruple evaporators, as described under (a) *Beet Sugar Manufacture* (p. 217), are not employed for concentrating the liquors, vacuum pans being always used. If large grain be desired, when the pan is nearly full a considerable portion of its contents is allowed to run out, and the valve is then closed. Fresh liquor is now introduced until the pan is again nearly full, and, the boiling being continued, the sugar from this is deposited upon the surface of the crystals left in the pan. This operation, known as 'cutting,' is repeated several times, yielding each time larger and larger grain. It is generally the practice to raise the temperature of the massecuite 10° to 15°F. before discharging or 'letting-go' to render the mass less viscous. When large crystals are required, crystals are often put in the pan with the first liquor. If the object be to produce soft sugars, or 'pieces,' a larger quantity of liquor or of syrup from a previous operation is introduced into the pan, and on this being boiled down to the crystallising point, yields a greater number of small crystals, each of which, acting as a centre of crystallisation, lessens the time of boiling, thereby producing a massecuite of smaller grain. The larger crystals are boiled at a comparatively high temperature, from 160° to 190°F., and the 'pieces' at from 120° to 140°F. The time of boiling, in the former case, is about three times longer than in the latter. A pan of crystals will thus take from 8 to 12 hours to boil, whilst a pan of pieces or loaf-sugar will take from 2½ to 4 hours, the time varying with the heating surface of the pan, the density of the liquor, &c.

(6) *Separation of the crystals in the centrifugal machines.* On leaving the vacuum pan, the massecuite passes into the 'heaters.' These are either made cylindrical, or in the shape of a trough, and are generally fitted with stirring gear, being also sometimes heated with steam jackets. In the refinery various means are employed to convey the massecuite from the heater to the centrifugal machines. Metal trucks running on rails are often used, each being large enough to charge one centrifugal machine. The truck is run below the heater, and a valve at the bottom of the latter is then opened until the truck is full of massecuite. The full truck is next run over the top of a centrifugal machine, which has been already set in motion, and is running at a somewhat low speed. A sliding valve at the bottom of the truck is now opened, and its contents fall into the moving machine. The velocity is then increased, and a little water is sometimes added towards the end of the operation to assist in washing out the adhering syrup. When the sugar is deemed to be sufficiently dry, the machine is stopped, and the sugar is removed through openings in the bottom of the machine, which have been closed up during the machining, or it is sometimes taken out from the top.

If the massecuite machined is of low quality, the resulting sugar, on leaving the machine, is allowed to fall upon a riddle which is kept moving backwards and forwards, and any syrup knobs are broken up by hand and mixed with the rest of the sugar.

The syrup from the centrifugal machines is again concentrated and yields another crop of sugar; or it is mixed with the 'bag-washings' and the 'sweet-water' from the char, and used for making a lower quality of raw liquor.

In many of the Scotch, and also in some English refineries, no molasses is turned out, but the syrup resulting from the last products of one day is returned to form part of the next day's melting. To work this system with success it is necessary to employ raw sugars of a good description. The products of this mode of working are a first, second, and sometimes a third quality of white sugar in the form of small crystals, and two or three lower kinds of what is known as 'moist sugar' or soft 'pieces,' to be mentioned further on.

The use of this system favours the production of a large turn-out, owing to the rapidity with which the sugar is refined, the first product being often ready for sale the day after the raw sugar has entered the refinery, and the remaining products within two or three days.

Having described the process of refining as far as the production of the massecuite and the separation of the crystals in the centrifugal machine, the methods used in the manufacture of: (*a*) loaf; (*b*) cube; (*c*) granulated; (*d*) crystal; (*e*) yellow crystals; (*f*) soft pieces, and (*g*) castor and icing sugars will now be given.

(*a*) *Loaf sugar*. Liquor of good quality is boiled in a vacuum-pan to a fine-grained thick massecuite, which, after being heated in a steam-jacketed heater to about 180°F., is run into conical sheet-iron moulds. The moulds are placed on the floor at the basement of the refinery, the room being termed the 'fill house.' They are arranged in rows, touching and supporting each other. Before being filled, the small hole at the pointed end, or nose, of each mould is closed by means of a screwed-up rag, or, better, by a wooden spigot. The moulds remain in the fill-house from 10 to 12 hours, during which their contents are stirred up until the mass becomes thick and there is no danger of the crystals settling out and so rendering the loaf of unequal texture. When their contents are set, the moulds are removed to one of the upper floors of the refinery, and the plug closing the hole in the nose of each mould being removed, a pointed iron rod is inserted into the sugar to the depth of 2 or 3 ins. to facilitate the drainage of the syrup. The moulds are next placed in holes in racks or stages, and the so-called 'green syrup' drained away into gutters placed beneath. The stages are generally made of wood, and the holes are arranged at such a distance apart that the rims at the top of the moulds may touch and afford mutual support. After remaining on the stages for about 24 hours the green syrup ceases to run, and the soft surface of the sugar is then removed, and mixed with a perfectly colourless and nearly saturated solution of sugar (fine liquor) forming a magma which is then replaced in the mould, thus making a flat, porous surface, through which the fine liquor, afterwards employed for washing the sugar, passes in a slow even stream. By this means the danger of the fine liquor taking a short passage through the loosest part of the loaf is avoided. When the surface of the magma has become dry more fine liquor is run on, and this operation is repeated several times until the syrup running away is colourless. When such is the case, the sugar is allowed to drain until only a few inches of the pointed end or nose remains in a moist state; the syrup from this may be removed by suction or centrifugal force, but the usual practice has been to cut the moist end off. The upper surface of each loaf must also be removed, the sugar obtained in each of these operations being used for making fine liquor. The loaves are now taken from the moulds by inverting the latter and striking them on the rim against a hard block of wood. Each loaf is next placed on its base, in racks, one above the other, heated by steam pipes or hot air to about 120°F. Sometimes the loaves are covered with paper before they are dried in the stove to avoid the danger of cracking through accidental currents of cold air. The time occupied in these various operations depends in a great measure upon the quality of the raw sugar employed, and the grain of the fine sugar produced, but it may generally be said that the process from beginning to end occupies from 10 to 14 days, and that the sugar is for about half this time in the stoves.

(*b*) *Cube sugar*. Attention has been directed to the importance of finding some more rapid mode of working, and the result has been that numerous inventions have been brought out and patented for this purpose. These inventions may be divided into two classes, (1) those producing moulded sugar from massecuite in the form of slabs or sticks; and (2) those producing sticks or cubes of sugar, by means of pressure, from soft white sugar which has been dried and purified in a centrifugal machine. Under the first named category, the most important is Langen's process. In this the massecuite is run into small segmental moulds divided every ⅞ in. or so by means of movable iron plates. The moulds are placed one upon another, with a perforated plate, the edges of which are covered with cloth, to make a joint, and they are held down to the top of an iron truck. They are then filled, and allowed to remain till the sugar has set, when the moulds are taken apart and placed in a special centrifugal machine, by which the green syrup is removed. Then they are taken to another centrifugal machine, in which the sugar is washed by fine liquor, this process being repeated, if necessary. These two operations are sometimes effected in the same machine. The sugar slabs are afterwards dried in a stove and cut up into cubes. In the Adant process, a modification of Langen's, the principal advantage is that the slabs are placed edgewise in the centrifugal, their removal thus being rendered easier. Duncan and Newlands have also devised a plan of producing moulded sugar, in the form of sticks, which has been somewhat largely used.

(2) The principal processes in use for making pressed cubes are those of Hersey and of Pzillas. By means of the Hersey cube machine (Fig. 21), cubes are made in the following way: Perfectly white moist sugar of good quality from the centrifugal machine is fed into the hopper at the top of the machine, and is then automatically mixed with a small quantity of liquor, just sufficient to cause the grains to bind together. At the bottom of this hopper is a hollow revolving drum, in the periphery of which are rows of moulds, each of the size of the cube it is intended to make These moulds are open at the top, but are closed at the bottom by movable plungers connected together by iron bars placed parallel

with the axis of the drum. These bars are caused to advance or retreat by means of a cam arrangement. The sugar falls from the hopper into the row of moulds which happens to be under it, and in which the plungers are withdrawn by the action of the cams to their fullest extent; the drum then moves, causing another row of empty moulds to receive their charge. The full moulds pass behind an iron 'press plate,' extending about half way round the drum, which closes up the top openings, and against this plate the sugar is gradually squeezed, by means of the plungers, until the filled moulds reach the bottom of the press plate, when the cubes are pushed out in rows on to small tin plates, which are carried on a band moving in unison with the drum. The plates containing the comparatively soft moist cubes are then placed in a stove heated by steam pipes, and the sugar on drying becomes hard enough to pack into barrels. The greater portion of the hard sugar consumed in the United States is made by this process. One such machine will convert 250 tons of soft sugar into cubes, weekly, with a comparatively small amount of manual assistance.

The Pzillas cube machine, which is largely used on the Continent, was invented prior to the last-described machine, and resembles it in many respects. The sugar, however, is turned out in the form of sticks, and requires to be cut into cubes by means of a cutting-machine. This latter consists of a table on which the sticks, after being arranged side by side, are moved by an endless band, passing on their journey between knives having a reciprocating movement, causing them to cut the sugar into cubes or tablets. Other machines have been devised for pressing sugar, but as they have not come into general use, it is only necessary to say that most of them consist of tables on which are placed metallic plates perforated with square holes which are filled with soft sugar, and are then automatically moved under a plunger, the bottom of which is made with cube-shaped projections which fit into the holes in the plate and press the sugar. The plate is then moved on again over a portion of the table which is perforated in a similar way, and the cubes are pushed through the holes, by means of plungers, on a travelling band.

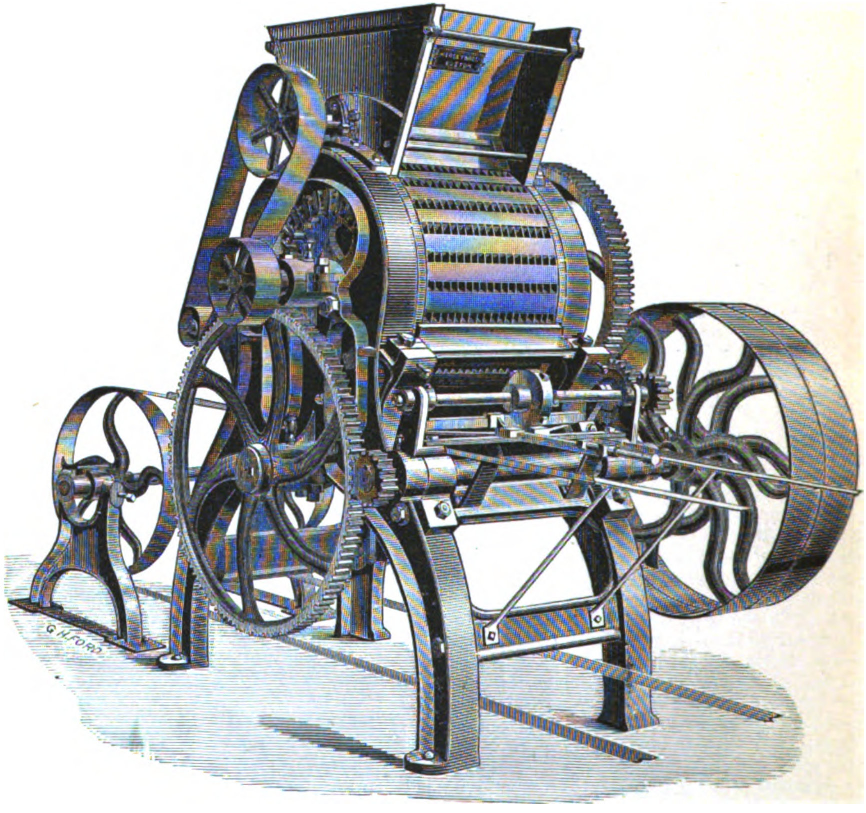


FIG. 21.—HERSEY CUBE MACHINE.

(c) *Granulated sugar*. An important process for drying or granulating sugar, known as the 'Hersey granulating process,' is now in operation in almost every refinery in the United States and Canada, and is also adopted in many refineries in Europe and elsewhere. The machine employed for this purpose is illustrated in Fig. 22, which shows a longitudinal section through the centre of the machine, and a transverse section on the line AB, seen in the longitudinal section.

The heating-cylinder—which is situated inside the conveyor-cylinder and revolves with it—is filled with steam through a pipe in one end; and the water of condensation is delivered from the opposite end, through a discharge pipe, so that the heating-cylinder is always full of steam.

The sugar is fed at one end through a spout by a set of rolls placed above the machine, or by a screw-feed; and by lifting-shelves placed on the inside of the outer cylinder, it is carried up and dropped in a continuous shower upon the heating-cylinder, and rolled off by the rotation of the machine, to be again carried up, working forward to the opposite end by the inclination of the apparatus, and there delivered into a screen for separating into the different grades. The heater-cylinder is placed centrally within the conveyor-cylinder, and is adjusted and secured by means of suitable adjusting screws. The conveyor-cylinder is made of iron; and the heater of steel plate. The conconveyor-cylinder is 23 ft. long and 6 ft. in diameter, with the heater-cylinder 20 ft. long and 3 ft. in diameter, and makes six revs. per minute. There is a striker for the purpose of removing any sugar that may adhere to the cylinder on first entering the machine, and it is worked by cams. The machine is made to rotate by means of gearing upon the outside of the conveyor-cylinder, driven by a pinion on a shaft. The current of air constantly passing through the machine carries off the moisture from the sugar through an exit pipe.

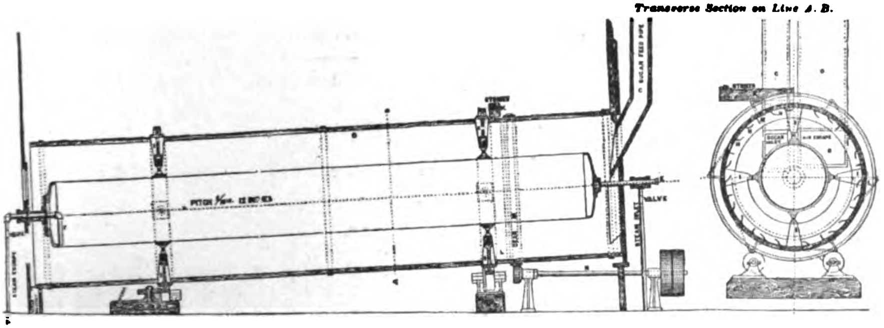


FIG. 22.—HERSEY GRANULATOR.

One important feature of the machine is that the sugar being delivered from the end into which the cold air is passing is cool, so that it does not cake, and can be immediately barrelled, and will not cause the barrels to shrink. The sugar being granulated or dried, not so much from extreme heat but by the moisture being constantly carried from the machine, is brought out clear and white.

(*d*) *Crystal sugar.* This class of sugar is produced by boiling the contents of the vacuum pan to about the same size of grain as in the case of that required for granulated. When this is done, half the massecuite is 'struck out,' and its place taken by fresh liquor, which is gradually drawn in, boiling being recontinued, so that the existing crystals increase in size, instead of fresh ones being formed. This operation is repeated, until the crystals attain the desired size after which the contents of the pan are 'let go,' being finally machined in the usual way.

(*e*) *Yellow crystals.* This sugar is made either from refined crystal, or from raw 88° beet sugar of good colour, previously washed in centrifugals with steam or water, by simply mixing with about 2 p.c. of golden syrup and a minute amount of Newlands' 'Golden Bloom' (Boake, Roberts and Co., Stratford, London). The mixing may be done by hand by spreading the sugar on a floor in a layer about a foot deep, watering it with the 2 p.c. of syrup and bloom, and turning the whole over with shovels; or it may perhaps preferably be carried out in a trough in which the sugar, syrup, and bloom are incorporated by means of a worm conveyor.

(*f*) *Soft pieces.* Soft pieces is a second quality sugar boiled from the syrup spun off the massecuite for granulated or for crystal sugar, after it has been passed over char. As a rule, 'soft pieces' is quite a low sugar, polarising less even than the raw sugar initially employed, but, of course, much improved in colour.

(*g*) *Castor and icing sugars.* Castor is a very small-grained granulated sugar; while icing is simply the finely ground and sifted lumps and pieces from the manufacture of cube and loaf sugars. There is, however, comparatively little trade done in these two products.

STATISTICS.

World's production of raw sugar. According to recently published reliable statistics (Board of Trade White Paper, 1911, No. 281), the estimated production of raw beet and raw cane sugar, for the entire world, during the years 1907, 1908, 1909, and 1910 inclusive, was as tabulated on p. 232.

Relative cost of production of beet and cane sugars. In the case of beet sugar, the cost of production is stated to be between 8*s.* 6*d.* and 9*s.* 10*d.* per cwt., depending upon the richness and quality of the roots, and the extraction in the factory. For cane sugar, the cost of production appears to vary from 6*s.* 6*d.* to 9*s.* 6*d.* per cwt., according to the country, the mode of

Raw Beet Sugar.

Country	1907 Tons	1908 Tons	1909 Tons	1910 Tons
Germany	2,206,012	2,104,358	2,045,805	2,004,653
Russia	1,391,923	1,522,384	1,522,041	1,255,345
Austria	1,001,686	1,116,707	1,079,473	1,225,589
Hungary	303,766	266,622	276,147	
Holland	201,819	176,035	215,224	191,691
Belgium	277,317	227,830	253,220	244,411
France	754,746	734,291	793,436	802,341
Sweden	150,798	110,138	134,497	124,959
Denmark	51,814	65,230	64,398	63,955
Italy	104,673	133,781	162,655	109,014
Spain	93,144	106,612	108,232	81,666
Other European Countries	29,174	34,862	37,675	45,595
Total for Europe	6,566,872	6,598,850	6,692,803	6,149,219
United States	432,234	413,950	384,010	457,562
Total estimated Quantity of Raw Beet Sugar produced in Europe and the United States	6,999,106	7,012,800	7,076,813	6,606,781

Raw Cane Sugar.

Country	1907 Tons	1908 Tons	1909 Tons	1910 Tons
In British Empire :—				
Mauritius	181,526	181,834	198,214	244,597
Commonwealth of Australia	217,479	165,715	147,470	149,334
Fiji	68,334	66,137	68,942	68,900
Natal	24,223	31,993	77,491	76,000
West Indies :—				
Jamaica	28,481	24,000	18,823	12,000
St. Lucia	5,364	4,982	5,518	5,500
St. Vincent	298	223	288	
Barbados	38,033	36,353	17,795	36,389
St. Christopher and Nevis	14,879	11,744	12,321	20,000
Antigua	14,774	13,316	9,171	
Trinidad and Tobago	50,564	48,933	45,330	44,139
Other West Indian Islands	504	223	70	75
British Honduras	615	605	410	400
British Guiana	100,737	115,212	108,533	101,843
British India	2,205,300	2,046,900	1,872,900	2,125,300
Total British Empire (including India)	2,951,111	2,748,170	2,583,276	2,884,477
In Foreign Countries :—				
United States	243,000	352,000	325,000	335,000
West Indies (other than British) :—				
Cuba	1,427,673	961,958	1,513,582	1,804,349
Other parts	348,461	393,356	426,083	503,953
South America	548,598	535,331	620,335	587,829
Dutch East Indies (Java)	1,062,795	1,114,186	1,189,420	1,200,618
Hawaiian Islands	464,677	477,190	489,357	462,613
Other Foreign Countries	599,105	636,861	710,688	881,624
Total Foreign Countries	4,694,309	4,470,882	5,274,465	5,775,986
Total estimated production of Cane Sugar	7,645,420	7,219,052	7,857,741	8,660,463

cultivation, and the methods of manufacture used (*cf.* International Sugar Journal, 1910, 12, 605, and 1911, 13, 7).

Consumption of sugar. From the statistics already quoted (Board of Trade White Paper, 1911, No. 281) the estimated consumption of sugar in pounds per head of population, in the principal countries of the world, is as follows:

Country	Description of sugar in which the particulars are expressed	1907 Lbs.	1908 Lbs.	1909 Lbs.	1910 Lbs.
United Kingdom	Raw and refined (net imports)	86·03	81·92	85·77	82·43
	In equivalent of refined	78·19	76·45	79·55	77·05
Germany	Refined	37·01	37·62	38·75	38·61
Netherlands	Refined	36·17	35·79	37·43	37·25
Belgium	Refined	25·98	27·24	28·33	29·12
France	Refined	32·28	32·85	33·92	34·13
Austria-Hungary	Refined	21·73	21·87	22·88	24·09
United States	Mainly raw sugar	81·19	74·11	80·43	79·90
Dominion of Canada	Raw and refined	70·24	67·03	66·46	Not yet available.
Commonwealth of Australia	Raw and refined	109·37	89·16	122·31	,,

LITERATURE OF SUGAR MANUFACTURE AND REFINING.

Books. Jones and Scard, The Manufacture of Raw (Cane) Sugar (Ed. Stanford, London, 1909); H. C. Prinsen Geerligs, Cane Sugar and its Manufacture (Norman Rodger, London, 1909); Noël Deerr, Cane Sugar (Norman Rodger, London, 1911); Lewis S. Ware, Beet Sugar Manufacture and Refining (Chapman and Hall, London, 1907); Newlands Bros., Sugar (Spon and Co., London, 1909); G. Déjonghe, Technologie Sucrière (Dunod and Pinat, Paris, 1910); P. Horsin-Déon, Traité théoretique et practique de la fabrication du sucre (Geisler, Paris, 1912); Stift and Gredinger, Der Zuckerrübenbau und die Fabrikation des Rübenzuckers (Hartleben's Verlag, Vienna and Leipzig, 1910); Gredinger, Die Raffination des Zuckers (Hartleben's Verlag, Vienna and Leipzig, 1908).

Journals. The International Sugar Journal, London; The American Sugar Industry, Chicago; The Louisiana Planter, New Orleans; Journal des Fabricants de Sucre, Paris; Bulletin de l'Association des Chimistes de Sucrerie, Paris; La Sucrerie Belge, Brussels; Revista Industrial, Tucuman; Centralblatt für die Zuckerindustrie, Magdeburg; Die deutsche Zuckerindustrie, Berlin; Zeitschrift des Vereins der deutschen Zuckerindustrie, Berlin; Österreichisch-Ungarische Zeitschrift für Zuckerindustrie, Vienna; Zeitschrift für Zuckerindustrie in Böhmen, Prague; Archief voor de Suikerindustrie in Nederlandsch-Indië, Soerabaia, Java.

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B. E. R. N.

SUGAR ANALYSIS.

The methods to be described in this article are selections from the most modern, which have been found to give accurate results in the writer's hands. Since they are all empirical it has been necessary to give a large number of tables. These, in most cases, have been condensed from the originals, so that intermediate values must be obtained by interpolation.

Qualitative reactions of the sugars. The power of reducing alkaline solutions of metallic salts (*see* pp. 246, 255) and that of forming phenylosazones (*see* p. 261), are exhibited by those sugars which contain a free carbonyl group. Some of the latter class of sugars form characteristic phenylhydrazones. Thus the phenylhydrazones of mannose, fucose, rhamnose, and rhodeose are very insoluble and separate almost immediately when a solution containing equal parts of phenylhydrazine and 50 p.c. acetic acid is added to a cold aqueous solution of either of the above sugars. The use of substituted derivatives of phenylhydrazine as reagents for identifying different sugars is often of service both as regards the formation of hydrazones and of osazones. Methylphenylhydrazine gives a characteristic osazone with lævulose, but does not form an osazone with dextrose or mannose. The sugars also give characteristic colour reactions with different phenols. For a description of these and other reactions the reader is referred to the article on CARBOHYDRATES (vol. i. p. 631).

Polarimeters. The theory and construction of polarimeters are dealt with in a special article on POLARIMETRY (vol. iv. p. 309). The article, however, deals exclusively with instruments in which the rotation of the plane of polarised light is measured by rotating the analyser, and no description is included of those instruments, exclusively used in sugar technology, in which the rotation is measured by quartz compensation. These instruments are generally known as saccharimeters, because their use is restricted to sugars, and more especially to sucrose (cane sugar), for which they were originally designed. It was the French physicist, Soleil, who in 1848 devised a method of determining the strength of sugar solutions polarimetrically which would obviate the use of monochromatic light, which presents many inconveniences and difficulties in practical work. Soleil's method was based on the fact that the rotation of the plane of polarised light by solutions of sucrose and by solid rock crystal (quartz) respectively, runs approximately parallel for light of different degrees of refrangibility. In other words, solutions of sucrose and solid rock crystal have substantially the same rotatory dispersion. Soleil therefore constructed an instrument in which the polariser and analyser were fixed, and in which the rotation of the plane of polarised light by a sugar solution could be compensated by means of a definite thickness of quartz rotating the plane in the opposite direction. The principle of this method of compensation may be seen by the aid of the following diagrams.

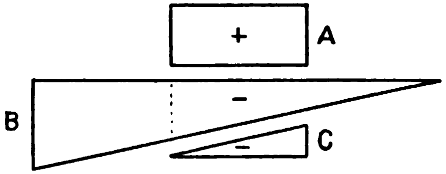

Fig. 23.

In the single-wedge system, Fig. 23, the plate A of dextro-rotatory quartz is stationary, whilst the wedge B of lævo-rotatory quartz is capable of being moved in a lateral direction, and the wedge C of lævo-rotatory quartz is again stationary. The system as arranged in the diagram is at the zero-point, that is to say the two lævo-rotatory quartz wedges exactly compensate the dextro-rotatory quartz plate. If now a dextro-rotatory sugar solution is placed in the instrument and the equilibrium thereby destroyed, the movable lævo-rotatory quartz wedge B is moved from left to right until the alteration caused by the sugar solution is exactly compensated. Obviously by employing a plate and wedges the rotation of which is of opposite sign, an instrument for lævo-rotatory sugars might be constructed.

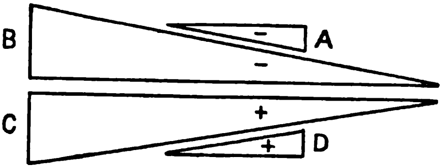

Fig. 24.

The double-wedge system, Fig. 24, is adapted for either dextro- or lævo-rotatory sugars. It will be seen that in this system there is no quartz plate but two small wedges A and D of opposite rotation, which are fixed, and two large wedges, B and C, also of opposite rotation, which can be moved in a lateral direction as already explained.

The earliest instruments to which the principle of quartz compensation was applied were the Soleil-Duboscq in France, and the Soleil-Ventzke Scheibler in Germany. In both these instruments the measurements are made in terms of the mean yellow ray. Two half discs of quartz of opposite rotation, cut perpendicularly to their optic axes, and each having a thickness of 3·75 mm., are cemented together. If such a plate be interposed between two Nicol prisms the principal planes of which are parallel, and white light be passed through the system, the two halves of the field will be of a uniform rose colour, due to the blending of the spectral colours, minus the yellow which is extinguished. The slightest rotation of the analyser (or in the case of quartz-compensating instruments, movement of the quartz wedge) will change one half of the field to blue, and the other to red, or *vice versa*. This is the so-called transition tint, which is complementary to the medium yellow or *jaune moyen* of Biot. If a sugar solution be placed in an instrument employing this device, the equilibrium in colour of the transition tint will be destroyed and can only be restored by rotating the analyser a certain number of degrees or by quartz compensation.

In former times most of the measurements of specific rotatory power were made in terms of this transition tint, the results being denoted by the symbol $[\alpha]_j$ (j=French *jaune*).[1] For a full discussion of the principle of these instruments the reader is referred to special works. Instruments employing the transition tint have, however, long since ceased to be used generally. Among their disadvantages is the fact that they cannot be used by those who are colour blind, and moreover in sugar technology one of the chief reasons for their abandonment is the difficulty of examining coloured solutions with them.

Modern double-field saccharimeters are the so-called penumbra or half-shadow instruments, employing white light and quartz compensation. Two of these may be mentioned, namely the German instrument of Schmidt and Haensch, and the French instrument of Laurent. The first is constructed for the Ventzke scale, whilst the second employs the French scale. The principles of both of these scales will be dealt with later.

In the earliest form of the German instrument, the half shadow effect is produced by the use of a Jellet-Cornu prism as polariser (Jellet, Report British Assoc. 1860, 13; Cornu, Bull. Soc. chim. 1870, [ii.] 14, 140). An ordinary Nicol prism is divided into halves along its whole length corresponding to the plane of the shortest diagonal. A small wedge $\alpha/2$ is ground from the surface of each half, and the two are then reunited by means of Canada balsam. This makes a double Nicol prism which has two principal planes, making the half-shadow angle α with an ordinary Nicol prism as analyser, the principal plane of the latter being set at right angles to the bisectrix of the principal planes of the divided prism. In the Laurent instrument the half-shadow effect is produced by means of a half disc of quartz (*see* vol. iv. p. 317). The Lippich prism is now more generally used as polariser in the German instrument. By its means a triple field is given (see vol. iv. p. 318).

The Schmidt and Haensch half-shadow saccharimeter with Jellet-Cornu prism as polariser is shown in Fig. 25.

The more modern form of the instrument, furnished with a Lippich polariser, is shown in Fig. 26. This particular instrument has the double-wedge system of compensation, the wedges being protected in a case.

Saccharimeters are furnished with an arbitrary scale, which gives percentages of sucrose direct when a solution of definite concentration is examined in a tube having a length of 2 dm. The weight of pure sucrose which dissolved in

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[1] For the relation of readings on this scale to those when sodium light is employed, see p. 237.

water and made up to 100 c.c. gives a reading of 100 divisions when examined in a 2-dm. tube is called the normal weight. The German and French instruments employ different normal weights.

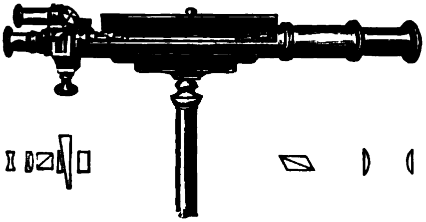

FIG. 25.

Saccharimetry—Ventzke, or German scale. With the object of dispensing with weighing in saccharimetric work, Ventzke took as his normal solution one of sucrose, which had a sp.gr. of 1·1 at 17·5°/17·5°, his idea being that since such a solution possesses unit excess gravity, the percentage of sucrose might be determined in a solution having approximately the concentration of the normal by taking its polarimetric reading in a 2-dm. tube and its specific gravity. It was soon found, however, that as the mineral matters and organic matters other than sucrose present in raw sugars had a different effect on the specific gravity than had sucrose, such a method was inaccurate. A solution of sucrose of the above specific gravity contains 26·048 grms. of sucrose dissolved in 100 Mohr's cubic centimetres.[1] The Ventzke normal weight when metric cubic centimetres are employed is 25·9872, or for practical purposes 26 grms. The International Commission, at its third meeting in Paris in 1900, recognising the confusion arising from the two standards of volume, recommended the abandonment of the Mohr for the metric cubic centimetre, and they also recommended that all readings should be made at 20°C. The change in temperature from 17·5°C. to 20°C. necessitated a recalculation of the normal weight owing to the difference in the specific rotations of sucrose and quartz at these two temperatures. The normal weight thus found is 26·0082 grms., and it was decided to fix it at 26 grms.

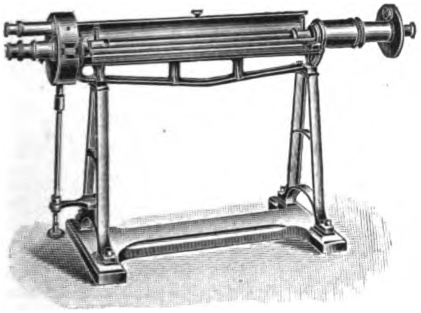

FIG. 26.

The normal weight used in the scale adopted by saccharimeters of French manufacture was fixed in 1896 at the meeting of the International Congress of Applied Chemistry in Paris as 16·29 grms. of sucrose dissolved in water and made up to 100 metric cubic centimetres at 20°C. If Mohr's cubic centimetres are used the normal weight was fixed at 16·33 grms.

It is a fact known to all who are engaged in accurate saccharimetric work that the normal weights of different saccharimeters vary, and that it is always necessary to determine the exact weight for each instrument. The German firm, Messrs. Schmidt and Haensch, are, however, particularly careful in the graduation of their scale, as may be seen from the following extract from a letter addressed to Dr. C. A. Browne (*see* A Handbook of Sugar Analysis, 1912, p. 117).

'The establishment of the scale divisions of our saccharimeters is made at a temperature of 20°C. After fixing the zero-point the linear distance of the 100-degree division is determined by means of a normal quartz plate reading exactly 100 degrees, and standardised at the Physikalisch-Technische Reichsanstalt. This linear distance is then divided into 100 exactly equal parts, the intermediary divisions being also verified by means of corresponding normal standardised quartz plates. The surfaces of the quartz wedges are made perfectly plane, so that a quartz stratum of half thickness corresponds to a half value in the division. Slight errors cannot be prevented, as it is impossible to obtain quartz wedges of the necessary length which are absolutely optically homogeneous throughout. The variableness in the specific rotation of sucrose with concentration of solution is not taken into consideration in the establishment of the scale division, and this must be corrected for by calculation. Aberrations in the scale division caused by impurities in the quartz can be detected by the control observation tube.'

Verification of the saccharimeter scale. For this purpose accurately ground quartz plates, standardised by the Physikalisch-Technische Reichsanstalt can now be obtained, but it is obviously prohibitive to purchase a sufficient number of these to check the entire scale. It is, moreover, desirable that this shall be done by means of solutions of pure sucrose of different concentration. Commercial sucrose, although of a high degree of purity, cannot be employed for this purpose, but it must be purified as follows. A concentrated solution of the purest loaf or cube sugar is prepared at the lowest possible temperature. This is further concentrated by evaporation under a partial vacuum, such that the boiling-point never exceeds 80°C. The syrup is then thinned down to twice its volume with a little redistilled commercial alcohol, mixed in a Winchester quart bottle with two to three times its volume of redistilled commercial alcohol, and the mixture vigorously shaken until the crystals separate in the form of

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[1] The Mohr cubic centimetre, introduced in 1855, is the volume occupied by 1 gram of water at 17·5°C., weighed in air with brass weights. The writer of this article has, for many years, employed the fluid gram at 15·5°C. for all volumetric determinations except those which concern gas analysis. The advantages are that the instruments can be so readily checked, and that specific gravities are usually taken in commercial laboratories at 15·5°/15·5°.

a magma. These crystals are filtered from the mother liquor on a Buchner funnel, washed with alcohol, again dissolved in water, and the operations repeated. After two precipitations the sugar is usually pure. It should be dried on a porous plate over sulphuric acid in a vacuum desiccator, and finally heated for a short period at 80°C. The sugar so prepared should then be examined in various ways to ascertain its purity. The mineral matter should be estimated on at least 10 grms. (*see* p. 262), its behaviour towards Fehling's solution should be ascertained, and the specific rotatory power should be determined in a polarimeter making use of sodium light, in which the measurement is made by rotation of the analyser.

The scale having been checked with sugar solutions of different concentration, or by the control tube (*see* below), and the results corrected for the different conditions as described below, any further checking of the instrument can be accomplished by means of standard quartz plates.

One of the most convenient ways of checking the scale of a saccharimeter is by means of the Landolt control tube, the latest form of which, as sold by Schmidt and Haensch, is illustrated in Fig. 27.

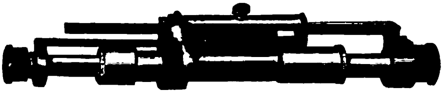

FIG. 27.

The tube can be adjusted to any length from 220 to 420 mm. by means of a telescopic arrangement. The length of a solution is read off on a scale by means of a vernier to 0·1 mm. A funnel is used to receive the overflow of solution as the tube is shortened. For filling the tube the funnel is removed and the opening closed by means of a plug. The tube is then drawn out to its full length, and after moving one of the caps, filled in the usual way.

The following is the way in which the tube is used. A sugar solution is prepared of such a concentration that it gives a reading of 100 divisions at a length of about 400 mm. This will serve to test the scale at a point a few divisions above 100, and at all points below 100 to 55. For further information the reader is referred to Landolt (The Optical Rotating Power of Organic Substances, 1902, p. 441).

In verifying a saccharimeter by means of sucrose, account must be taken of the effect of concentration on the specific rotatory power of that sugar. The useful table shown in the next column has been calculated from the independent experiments of Schmitz and of Landolt by Browne (Handbook of Sugar Analysis, 1912, p. 118).

When cane sugar solutions are examined in a quartz compensating polarimeter with white light, errors due to the difference of rotatory dispersion of cane sugar and quartz produced by light of higher refrangibility are introduced. In order to eliminate this source of error Schönrock (Zeitsch. Ver Deut. Zuckerind., 54, 521) suggests that the white light should be filtered through a layer of 1·5 cm. thickness of a 6 p.c. solution of potassium dichromate.

TABLE I.—*Effect of Concentration of Sucrose on Saccharimeter Readings.*

Scale division.	Concentration grams sucrose, 100 true cubic centimetres, 20°C.	Specific rotation sucrose, 20°C.	Actual sucrose value of scale division.	
			By Landolt's formula.	By Schmitz's formula.
100·00	26·00	66·502	100·00	100·00
96·00	24·96	66·506	96·00	95·98
95·00	24·70	66·507	94·99	94·98
90·00	23·40	66·510	89·99	89·97
85·00	22·10	66·513	84·99	84·96
80·00	20·80	66·514	79·99	79·95
75·00	19·50	66·515	74·99	74·94
70·00	18·20	66·516	69·99	69·93
65·00	16·90	66·515	64·99	64·92
60·00	15·60	66·514	59·99	59·92
55·00	14·30	66·511	54·99	54·92
51·00	13·26	66·509	50·99	50·92
50·00	13·00	66·508	50·00	49·92
45·00	11·70	66·505	45·00	44·92
40·00	10·40	66·500	40·00	39·92
35·00	9·10	66·495	35·00	34·92
33·00	8·58	66·492	33·00	32·93
32·00	8·32	66·491	32·01	31·93
30·00	7·80	66·489	30·01	29·93
25·00	6·50	66·481	25·01	24·94
20·00	5·20	66·474	20·01	19·95
15·00	3·90	66·465	15·01	14·96
10·00	2·60	66·456	10·01	9·97
6·00	1·56	66·443	6·01	5·98
5·00	1·30	66·442	5·00	4·98

Effect of temperature. This effect in the case of a quartz compensating instrument, apart from the change in the specific rotation of sucrose at different temperatures, is threefold as shown by Schönrock (*l.c.*). Thus: (1) the change in shape of the quartz wedge by expansion or contraction; (2) the change in the specific rotation of quartz; and (3) the change due to the expansion or contraction of the material of which the scale is composed. For quartz compensating Ventzke saccharimeters, having a scale of the alloy, nickeline, the polarisation value at any temperature P^t of a sugar solution is $P^t = P^{20^\circ}[1+0{\cdot}000148(t-20)]$. When the scale is etched on the quartz wedge, the correction coefficient is 0·000130. C. A. Browne (*l.c.*, p. 127) has compiled some very useful data on the effect of temperature in saccharimetry. He points out that the increase in the reading of quartz with the temperature produces a lowering of the saccharimetric readings, since a lesser thickness of quartz is required for compensation. With sugars which undergo a decrease of rotation with increase in temperature, the combined influences of quartz and sugars are in one direction, and the error introduced may be considerable. Thus with sucrose the temperature coefficient at 10°C. is (0·000148+0·000242), at 20°C. it is (0·000148+0·000184), and at 30°C. it is (0·000148+0·000121)

The following table giving the variation in the Ventzke reading per 1°C. according to different observers, is quoted from Browne's treatise.

Andrews (Technology Quarterly, Mass. Inst. Technology, May (1889), 367)	0·0300
The United States Coast and Geodetic Survey	0·0293
Wiley (J. Amer. Chem. Soc. 21, 568)	0·0314
Prisen Geerligs (Archief Java Suikerind, July, 1903)	0·0300
Watts and Tempany (West Indian Bull. vol. iii. p. 140)	0·0310
Average	0·0303

The average temperature coefficient 0·000303 is thus very close to Schönrock's value for 25°C. (0·000148+0·000152)=0·000300. For temperatures between 20° and 30° C. the general equation $P^{20^\circ}=P^{t}\,1+0{\cdot}00030\,(t-20^\circ)$ may be used for correcting Ventzke readings to 20°C.

The temperature coefficients of other of the better known sugars for readings on the Ventzke scale have been calculated by Browne, and are given in the following table :—

TABLE II.—*Temperature Co-efficients of Different Sugars of Ventzke Scale.*

Sugar.	A. $[\alpha]_D^{20^\circ}$	B. Change in $[\alpha]_D^{20^\circ}$ for 1°C. increase.	C. Temperature coefficient $\frac{B}{A}$.	Temperature coefficient of reading upon Ventzke scale for 1°C. increase. C+coefficient for quartz (−0·000148).	
Fructose	−92·50	+0·625	−0·006757	−0·006905	→ 0
Invert sugar	−20·00	+0·312	−0·015600	−0·015748	→ 0
Lactose	+52·53	−0·070	−0·001332	−0·001480	0 ←
Maltose	+138·04	−0·095	−0·000688	−0·000836	0 ←
Glucose	+53·23	No change.	No change.	−0·000148	0 ←

In the case in which a mixture of sugars is examined in a saccharimeter, the combined influence of the temperature coefficients of each sugar must be taken into account.

In order to obviate errors arising from inequalities of temperature in polarimetric work where great accuracy is required, the readings are conducted in a chamber kept at a constant temperature.

C. A. Browne (*l.c.*, p. 145) has calculated the following useful table, showing the relation between the Ventzke sugar scale, the French sugar scale, and degrees of arc (sodium light)—

Scale.	Equivalent.
1° Ventzke sugar scale=0·34657°	angular rotation D.
1° angular rotation D =2·88542°	Ventzke sugar scale.
1° French sugar scale =0·21666°	angular rotation D.
1° angular rotation D =4·61553°	French sugar scale.
1° French sugar scale =0·62516°	Ventzke sugar scale.
1° Ventzke sugar scale=1·59960°	French sugar scale.

The factor for converting divisions of the Ventzke scale into angular degrees (sodium light), differs slightly for the different sugars. Thus Landolt (Ber. 21, 194) gives the following factors for five sugars—

Sucrose	0·3465
Lactose	0·3452
Glucose	0·3448
Invert sugar	0·3432
Raffinose	0·3450

Brown, Morris and Millar (J. Chem. Soc. Trans. 71, 92) give the following values—

Sucrose, 10 p.c. solution	0·3469
Maltose, 10 p.c. solution	0·3449
,, 5 ,, ,,	0·3457
Glucose, 10 p.c. solution	0·3442
,, 5 ,, ,,	0·3454
Starch products, 10 p.c. solution	0·3458
,, 5 ,, ,,	0·3454

Herzfeld (Ber. 28, 441), using a solution containing 11·29 grms. of anhydrous maltose in 100 c.c., found the value of the factor to be 0·3471. For ordinary practical purposes, the writer employs the factor 0·346 for converting divisions of the Ventzke into degrees of arc (sodium light) for all sugars.

The following table gives the rotation of some sugars in angular degrees and in divisions Ventzke as determined by Morris.

TABLE III.—*Rotation of some Sugars in* 10 *p.c. Solution at* 20°*C.*

(According to Morris (J. Fed. Inst. Brewing, 1898, 4, 174).)

—	$[\alpha]_D$	Reading in a 2 dm. tube in the half-shadow polarimeter employing white light. Ventzke divisions for 1 gram of sugar in 100 c.c.
Dextrin	202·0°	11·66
Maltose (anhydrous)	138·0°	7·97
Cane sugar	66·5°	3·84
Dextrose	52·8°	3·05
Lævulose	−92·0°	−5·31
Invert sugar	−19·6°	−1·13

For the specific rotatory powers of other sugars the article on CARBOHYDRATES (vol. i. p. 631) should be consulted.

Much of the older work is recorded in terms of the mean yellow ray $[\alpha]_j$ as measured by the transition tint. Indeed, in certain laboratories, transition tint instruments are still in use. To convert degrees $[\alpha]_j$ to degrees $[\alpha]_D$, the former must be multiplied by the factor 0·9. There has been, however, much confusion with regard to what is meant by the medium yellow ray. Thus Brown, Morris and Millar point out (J. Chem. Soc. Trans. 71, 86), that whereas the original medium yellow ray of Biot was that which was rotated 24° of arc, by a quartz 1 mm. in thickness, as measured by the transition tint, Montgolfier and also Landolt, when dealing with the medium yellow ray, refer to one having a decidedly higher refrangibility with a millimetre-quartz rotation of 24·5°.

Polarimeter tubes. The following illustration gives the tube most usually employed with the Ventzke instrument. It will be noticed that one end is considerably wider than the other. The object of this is to obviate the necessity of filling the tube completely, by which work can be conducted in a much more cleanly manner. Air bubbles collect in this wide end of the tube in a position outside of the field of vision.

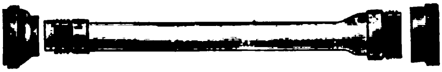

FIG. 28.

Polarimeter tubes are usually made of glass, but in some cases metal tubes are employed. These latter are not to be recommended on account of the fact that metal has a very much higher coefficient of expansion than glass.

The next illustration shows a tube which is furnished with a brass jacket in order that water may be circulated round the internal glass tube, which is T-shaped. This is for the purpose of controlling the temperature. The tube is filled by a funnel-shaped projection in the middle, which funnel also serves for the insertion of a thermometer to measure the temperature of the solution. Tubes of this kind are used in saccharimetry for the Clerget process (*see* p. 242).

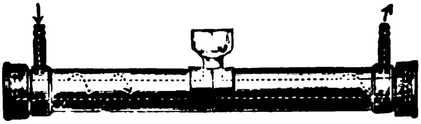

FIG. 29.

Methods for the polarisation of raw sugars. For this purpose the normal weight of the sample is dissolved in water, clarified with basic lead acetate, a little alumina cream added, the solution made up to 100 c.c., and the filtrate observed in a 2-dm. tube. The weighing out of the sugar is conveniently carried out in a special form of nickel boat. It is usual to dissolve the sugar at the room temperature.

Basic lead acetate is prepared in the writer's laboratories as follows: Lead acetate in fine crystals (150 grms.) is mixed in an evaporating basin with litharge (45 grms.) and water (25 c.c.). This paste is allowed to remain at the room temperature for 2–3 hours with frequent stirring. At the end of this time the lead acetate and most of the litharge have gone into solution. It is, however, gently warmed on a piece of wire gauze or a sand-bath by means of a burner. The cream, which is now quite limpid and devoid of colour, is poured into 500 c.c. of water and allowed to remain until the small amount of undissolved sediment settles out. It is desirable to filter the solution. The sp.gr. of the clear filtrate is about 1·20.

Alumina cream is made by pouring a cold 2–3 p.c. solution of alum contained in a pottle bottle into dilute ammonia of sp.gr. 0·98. The converse method of precipitation yields an unsatisfactory granular product. The alumina is allowed to subside and washed in the bottle by decantation twice a day until the supernatant liquid gives no reaction with barium chloride. This usually takes about a week.

The amount of basic lead acetate to be used varies with the kind of sugar. The purest centrifugal sugars require only from 0·5 to 2 c.c.; darker products require up to 10 c.c., whilst molasses require much more. The volume of alumina cream to be used for the normal solution is about 5 c.c.

The following rules were drawn up by the International Commission on Methods of polarising Raw Sugar (Paris, 1900):—

'In general all polarisations are to be made at 20°C.

'The verification of the saccharimeter must also be made at 20°C. For instruments using the Ventzke scale 26 grms. of pure dry sucrose, weighed in air with brass weights, dissolved to 100 metric c.c. at 20°C., and polarised in a room, the temperature of which is also 20°C., must give a saccharimeter reading of exactly 100·00. The temperature of the sugar solution during polarisation must be kept constant at 20°C.

'For countries where the mean temperature is higher than 20°C., saccharimeters may be adjusted at 30°C., or any other suitable temperature, under the conditions specified above, provided that the sugar solution be made up to volume and polarised at this same temperature.

'In effecting the polarisation of substances containing sugar employ only half-shade instruments.

'During the observation keep the apparatus in a fixed position, and so far removed from the source of light that the polarising Nicol is not warmed.

'As sources of light employ lamps which give a strong illumination such as a triple gas burner with metallic cylinder, lens and reflector; gas lamps with Auer (Welsbach) burner; electric lamp; petroleum duplex lamp; sodium light.

'Before and after each set of observations the chemist must satisfy himself of the correct adjustment of his saccharimeter by means of standardised quartz plates. He must also previously satisfy himself of the accuracy of his weights, polarisation flasks, observation tubes, and cover-glass. (Scratched cover-glasses must not be used.) Make several readings and take the mean thereof, but no one reading may be neglected.

'In making a polarisation use the whole normal weight for 100 c.c., or a multiple thereof, for any corresponding volume.

'As clarifying and decolorising agents use either sub-acetate of lead, alumina cream, or concentrated solution of alum. Bone-black and decolorising powders are to be excluded.

'After bringing the solution exactly to the mark at the proper temperature, and after wiping out the neck of the flask with filter paper, pour all of the well-shaken clarified sugar solution on a rapidly acting filter. Reject the first portions of the filtrate and use the rest, which must be perfectly clear for polarisation.'

At the seventh meeting of the International Commission for Uniform Methods of Sugar

Analysis, which met at the Columbia University, New York, in September, 1912, it was decided that in commercial analyses the use of temperature correction tables should be dispensed with, as far as possible.

Errors attending the use of basic lead acetate as a clarifying agent. These are threefold, *e.g.* precipitations of certain reducing sugars, especially lævulose, volume occupied by the precipitate, and the fact that in methods of inversion, such as the Clerget method, the stronger hydrochloric acid is replaced by the weaker acetic acid.

Sachs (Zeitsch. Ver Deut. Zuckerind. 30, 229) has devised the following method for correcting the error due to the volume occupied by lead acetate precipitate. The precipitate obtained by the clarification of a sugar solution is washed with cold and hot water until free from sugar. It is then transferred to a 100 c.c. flask, half the normal weight of sucrose added, and the solution made up to 100 c.c. The filtrate is polarised in a 4-dm. tube. The volume of the precipitate is then calculated as follows :—

$$v=\frac{100(P'-P)}{P'}$$

in which v is the volume of the precipitate, P the polarisation of the sucrose used, and P′ the polarisation of the sucrose with the precipitate.

Wiechmann (Proc. 5th Inter. Cong. Applied Chem. vol. 3, p. 118) determined the specific gravity of dried lead precipitates from various raw cane sugars in petroleum. His results are given in Table IV.

TABLE IV.

Sugar.	Weight of precipitate in grams.	Specific gravity H_2O =1·00.	Volume in cu. centimetres.
Jamaica Muscovado	0·4559	1·88	0·24
Maceio Muscovado	0·8112	1·65	0·49
San Domingo centrifugal	0·2525	2·91	0·09
Sandwich Island centrifugal	0·1378	2·84	0·05
San Domingo concrete	1·0139	3·80	0·27
Porto Rico molasses sugar	0·8959	4·35	0·21
Sandwich Islands	1·0195	4·38	0·23
Cebu mats	1·5400	2·17	0·71
Manila mats	1·3350	2·22	0·60

Horne (J. Amer. Chem. Soc. 26, 186) has suggested the use of dry basic lead acetate to obviate the error due to the volume of the precipitate. This is carried out as follows :—

The normal weight of sugar is dissolved in water in a 100 c.c. flask and made up to the mark without defecation. Small quantities of powdered anhydrous basic lead acetate are added to the solution until the impurities are nearly all precipitated. This point is as easily determined as in the defecation by a solution of the same salt. The organic and mineral-acid radicles in the solution combine with and precipitate the lead and lead oxide of the dry salt, whilst the acetic-acid radicle of the basic lead acetate passes into solution to combine with the bases originally united to the other acid radicles.

The results given in Table V show the very close agreement between the polarisations corrected by Sach's method, and by the use of dry defecation.

TABLE V.

Grade, country.	Ordinary polarisation.	Specific gravity of precipitate.	Volume of precipitate. c.c.	Corrected polarisation.	Dry lead polarisation.
Centrifugal	95·0	2·98	0·10	94·9	94·9
„ (mixed samples)	94·5	—	0·0765	94·43	94·4
„ Trinidad	96·95	2·91	0·0378	96·91	96·95
„ Java	97·425	2·30	0·0884	97·33	97·375
Muscovado, St. Croix	85·8	1·91	0·4118	85·45	85·5
Molasses sugar, Cuba	89·4	3·20	0·39	89·05	89·0
„ „	89·225	2·85	0·4204	88·85	88·85
„ „	86·45	1·96	0·7108	85·84	85·95
„ „	90·675	3·20	0·3204	90·39	90·45
„ „	89·35	—	0·8500	88·59	88·775
„ „	89·4	3·01	0·4554	88·99	89·0
„ „ Cuba	88·4	2·64	0·4924	87·97	88·0

Pellet (Bull. assoc. chim. sucr. dist. 23, 285) contends that the increase in polarisation due to the volume of the lead precipitate is not as great as calculated owing to the decrease in polarisation caused by the retention of sucrose in the precipitate which frequently counterbalances the error due to the volume of the precipitate. Horne (J. Amer. Chem. Soc. 29, 926) has since shown, however, that there is no appreciable retention of sucrose when dry basic lead acetate is used in minimum quantity. A possible error, to which attention has also been called by Pellet, is that any lead which passes into solution by the dry defecation method will increase the volume by the solution.

Hall (Bull. 122, U.S. Bur. of Chem. p. 225) carried out a series of experiments on a Philippine mat sugar to ascertain the effect on the polarisation of increasing amounts of dry basic lead acetate. The lead dissolved in the clarified filtrates was determined and the dilution calculated by allowing an increase in volume of 0·22 c.c. for 1 grm. of dry basic lead acetate dissolved in 100 c.c. of the solution (*v.* Table VI.).

TABLE VI.

Clarifying agent.	Amount of clarifying agent used.	In 100 c.c. filtrate. PbO.	In 100 c.c. filtrate. Basic lead acetate.	Estimated dilution.	Polarisation.
		grms.	grms.	c.c.	
Basic acetate solution .	3·0 c.c.	0·2678	—	—	86·70
Dry basic acetate . .	0·5 grm.	Trace	—	Trace	Too dark to read
,, ,, . .	1·0 grm.	0·1530	(0·20)	0·05	86·50
,, ,, . .	2·0 grms.	0·7203	(0·94)	0·20	86·60
,, ,, . .	4·0 grms.	2·1078	(2·73)	0·60	86·50

On these results C. A. Browne (*l.c.*, p. 214) remarks as follows :—

'It is noted that with an estimated dilution of 0·2 c.c. instead of a decrease in polarisation, as would be expected, there is an increase. With an estimated dilution of 0·6 c.c. the reading is the same as that first obtained, so that the combined effect of the dry lead upon the precipitation of fructose, and upon the lowering of the rotation of the fructose in solution is seen to be most pronounced. With sugar-cane products the use of dry basic lead acetate to the point of satisfactory clarification would seem to involve no decrease in polarisation. With low-grade sugar-beet and other products, which are comparatively free from fructose, there is, however, a danger of too low polarisation, since there is no compensating influence for the dilution caused by the excess of lead sub-acetate dissolved.'

It has been shown by Bates and Blake (Bull. U.S. Bur. of Standards, 3, [1] 105) that the presence of a large excess of basic lead acetate solution exerts a large influence on the rotatory power of sucrose. The results given in Table VII. are some of those obtained with normal solutions of sucrose :—

TABLE VII.

Cubic centimetres of basic lead acetate solution (sp.gr. 1·25) per 100 c.c.	Differences in divisions Ventzke between the polarisation of a solution containing no lead, and one containing the volumes of lead mentioned in the first column.
2·0	−0·13
4·0	−0·06
6·0	0·00
8·0	+0·09
10·0	+0·19
20·0	+0·45
40·0	+0·77

Some commercial sugar products can be defecated by a solution of neutral lead acetate, which is generally used as a solution of sp.gr. 1·25. Herles (Zeitsch. Zuckerind. Böhmen, 13, 559; 14, 343; 21, 189) suggested basic lead nitrate as a clarifying agent, especially for low-grade products which are being dealt with by the Clerget method. The replacement of hydrochloric acid by nitric does not influence appreciably the velocity of the hydrolysis of sucrose. The volume of the lead precipitate is, however, largely due to that of the basic nitrate itself, and reducing sugars are precipitated by the reagent.

Heron (J. Fed. Inst. Brewing, 1, 113), and also Zameron (Bull. Assoc. Chim. Sucr. Dist. 16, 337), have suggested clarifying sugar solutions with hypochlorite. Insufficient work has been carried out to test the validity of this method, which *prima facie* does not seem one that could be recommended.

There are certain hydrosulphites on the market which are employed in factory work on the large scale for decolorising purposes. Two of these are known by the names of 'Blankit' and 'Redo.' It has been suggested that these should be used in the laboratory for decolorising sugar solutions. They introduce errors, however, by reacting with reducing sugars to form oxy-sulphonates (*see* Bryan, Bull. 116, U.S. Bur. of Chem. p. 76). Another hydrosulphite derivative, sold commercially as 'Rongalite,' is free from this objection. It is sodium formaldehyde sulphoxylate.

Purified animal charcoal has been used for decolorising sugar solutions, but the error introduced by the adsorption of sucrose is considerable.

The results shown in Table VIII. were obtained by Bryan (*loc. cit.*, p. 71) and indicate the effect of different clarifying agents on the polarimetric reading. The reading with alumina cream alone is taken as the true polarisation.

TABLE VIII.

Clarifying agent.	Amount of clarifying agent used.	Direct polarisation.
Alumina cream . .	5 c.c.	89·00°V.
Basic lead acetate solution .	3·5 c.c.	89·50°
,, ,, ,, .	7 c.c.	89·55°
Neutral lead acetate solution	3 ,,	89·20°
,, ,, ,,	6 ,,	89·20°
Basic lead nitrate solution .	4 ,,	89·00°
Dry basic lead acetate .	1·5 grms.	89·05°
Sodium hydrosulphite .	1 grm.	88·60°

Analysis of sugar beets. The estimations ordinarily made are the following: Percentage of sugar in the roots, percentage of sugar in the juice, and specific gravity of the juice (degree Brix). From these data are calculated the coefficient of purity from the formula 100S/B, where S is the sugar in the juice and B is the specific gravity of the juice in degrees Brix.

The writer has a record of many hundreds of analyses of sugar beets grown in different parts of England during the past three years. As will be seen from the following tabulated results the roots are quite up to the standard of those grown on the Continent:—

TABLE IX.[1]

SUGAR IN ROOTS.

Sugar content.	Percentage of total samples.		
	1910.	1911.	1912.
Below 12 p.c. . .	2	2	—
From 12–14 p.c. . .	14	4	—
„ 14–15 „ . .	—	—	4
„ 15–17 „ . .	65	56	20
„ 18–20 „ . .	11	36	76
Above 20 p.c. . .	8	2	—

PURITY OF JUICE.

Coefficient of purity.	Percentage of total samples.		
	1910.	1911.	1912.
Below 79 p.c. . .	2	1	—
From 80–85 p.c. . .	14	6	2
„ 86–92 „ . .	67	52	—
„ 86–90 „ . .	—	—	20
„ 91–93 „ . .	—	—	50
Above 93 p.c. . .	17	41	28

Method of sampling. In taking samples the field is divided longitudinally into strips and roots are lifted in diagonal lines from one end to the other of each of these strips. The roots, having been washed, cleaned, and topped, not less than half a dozen from each strip, and preferably more, should be taken for analysis.

There are several ways of estimating the sugar content of the roots, but each requires that an average sample shall be obtained of the roots reduced to pulp. In the writer's experience the best machine for this purpose is that made by Robert Kiehle of Leipzig, which is illustrated in Fig. 30. It stands about 3 ft. 7 ins. in height, and is capable of being screwed to the floor. A parallel slice is taken out of the centre by means of a rasp wheel, the root being fixed on a carrier and pressed against this wheel longitudinally while it is being rotated, which may be done either by hand or by other power. The pulp is collected in the box S.

In order to justify the soundness of the principle of taking a median longitudinal slice from the root, attention may be drawn to the fact that the percentage of sugar varies in different zones of the root. The following analyses of transverse sections of one and the same root (*see* Fig. 31),[2] made by the writer, illustrate this.

Estimation of the percentage of sugar in the roots. The following modification of the hot water digestion method is the one adopted by the writer. The normal weight of pulp is washed into a 200 c.c. Kohlrausch flask with about 150 c.c. of hot water. Basic lead acetate solution (6 c.c.) is then added, and the flask and contents are placed in a bath of boiling water to digest for half an hour. The contents are then cooled, 5 c.c. of alumina cream added, made up to a volume of 200 c.c. After well mixing, the extract is filtered and the filtrate polarised in a 2-dm. tube. The reading in degrees Ventzke doubled and multiplied by 0·994 (to correct for the volume occupied by the marc)[1] gives the percentage of sugar in the roots.

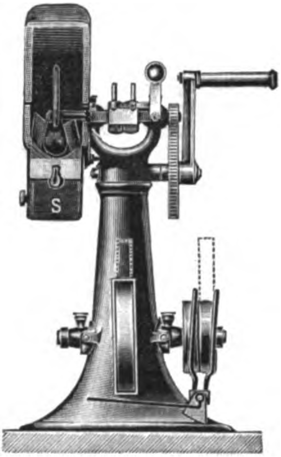

FIG. 30.

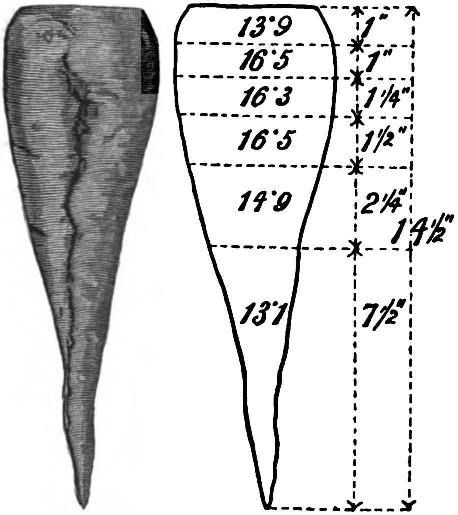

FIG. 31.

It is urged by some that digestion or

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[1] These results were published in an appendix by the writer to the Annual Report of the British Sugar Beet Council for 1912.

[2] This diagram is reproduced by the permission of the British Sugar Beet Council. See Annual Report, 1911, p. 17.

[1] This correction is not strictly accurate for all samples as the percentage of marc is subject to variation.

extraction with alcohol gives more accurate results than the aqueous digestion method; but, taking into account their inconvenience, these methods cannot be recommended for general purposes. It is not necessary to describe here in detail any of these methods, it will suffice to refer to the alcohol extraction method of Scheibler (Neue Zeits. für Rübenzuckerind. 2, 1, 17, 287; 3, 242) and the various hot and cold methods of digestion with water and with alcohol respectively.

Estimation of sugar in the juice. The juice having been expressed from a sample of the pulp enclosed in a filter cloth by means of a screw press, the normal weight is washed into a 100 c.c. flask, 2 c.c. of basic lead acetate solution, and 5 c.c. of alumina cream added, and the liquid made up to 100 c.c. The polarisation of the filtrate in a 2-dm. tube gives the percentage of sugar in the juice.

The specific gravity of the juice is determined by a Brix spindle, observing the usual precautions and correcting for temperature. The principle on which the Brix scale is constructed is explained on p. 265.

Estimation of lactose in milk by the polarimeter. For this purpose the Association of Official Agricultural Chemists, hereinafter referred to as the A. O. A. C., give the following method (Bull. 107, revised, U.S. Bur. of Chem. p. 118). The normal weight for hydrated lactose $C_{12}H_{22}O_{11},H_2O$ on the Ventzke instrument is 32·9 grms. Since the percentage of lactose in milk only amounts to 2–8 p.c., double this weight of milk is taken. Instead of weighing it is convenient to measure the milk, and the following table gives the volumes of milk at different specific gravity corresponding to 65·8 grms.

TABLE X.—*Volumes of Milk corresponding to the Double Normal Weight of Lactose.*

Specific gravity of milk.	Volume of milk for a lactose double normal weight (Ventzke scale).
	c.c.
1·024	64·25
1·025	64·20
1·026	64·15
1·027	64·05
1·028	64·00
1·029	63·95
1·030	63·90
1·031	63·80
1·032	63·75
1·033	63·70
1·034	63·65
1·035	63·55
1·036	63·50

It is pointed out that for ordinary purposes a pipette graduated to deliver 64 c.c. is sufficiently exact for all milks.

The milk is clarified with a solution of mercury nitrate, or with one of mercuric iodide. These are prepared as follows :—

Mercury nitrate. Metallic mercury is dissolved in twice its weight of nitric acid (sp.gr. 1·42), and the solution diluted with an equal volume of water.

Mercuric iodide. Potassium iodide (33·2 grms.) is added to a solution of mercuric chloride (13·5 grms.), dissolved in glacial acetic acid (20 c.c.) and water (640 c.c.).

The volume of milk equivalent to the double normal weight of lactose is measured into a flask having a mark at 102·6 c.c. For clarification either 1 c.c. of the mercuric nitrate solution may be used or 30 c.c. of the mercuric iodide solution (an excess of either reagent is without effect). The mixture is made up to a volume of 102·6 c.c., the 2·6 c.c. being the estimated volume of the precipitated casein and fat. After shaking, the liquid is filtered and polarised in a 4-dm. tube. The reading divided by four gives the percentage of lactose in the milk.

Other methods have been devised for the estimation of lactose in milk. Thus, Wiley and Ewell (Analyst, 21, 182), Leffman and Beam (Analysis of Milk and Mild Products, 1896, p. 39). Richmond has also dealt with the estimation of lactose in milk (*see* article on MILK, vol. iii. p. 533).

Lactose exhibits the phenomenon of mutarotation, and when solid products are polarised the solution must be allowed to remain until a constant reading is obtained, or the mutarotation must be destroyed by making up the solution in presence of a little alkali or ammonia. This applies to other sugars which exhibit mutarotation, *e.g.* dextrose, lævulose, &c.

Under special methods for the analysis of sugar mixtures, the use of the polarimeter in conjunction with cupric reduction methods will be described.

Method of estimating sucrose by double polarisation. The method of estimating sucrose in presence of invert sugar by determining the rotatory power before and after hydrolysis with acid was first suggested by Biot in 1842. It was made a practical one by Clerget in 1849 (Ann. Chim. Phys. [iii.] 26, 175), who elaborated a formula for calculating the results. Clerget's work is to be regarded as classical, and although the details of his original method have been revised, the constants which he established have remained practically unaltered. The method gives very satisfactory results with products of a certain degree of purity. With those of low purity, however (notably with molasses), in which there are many disturbing factors, the influence of which has not been fully worked out at the present time, the errors involved are considerable. In the writer's experience satisfactory results are to be obtained with raw beet sugars which give a direct polarimetric reading of 90 divisions and above on the Ventzke scale,[1] and with raw cane sugar giving a reading of 94 divisions and above on the same scale.

In the year 1888 a modification of Clerget's method was devised and elaborated by Herzfeld (Zeits. Ver. Deut. Zuckerind. 38, 699). It is carried out in the following manner.

The half-normal weight of sucrose is dissolved in 75 c.c. of water in a graduated 100 c.c. flask, 38 p.c. hydrochloric acid (5 c.c.) is then added, and the flask, in which a thermometer is inserted, is placed in a water-bath at 70°C. The flask is shaken continuously, and in this way the temperature of the solution is raised to 67°–70°C. in about 2½ mins., after attaining which it is

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[1] With these, however, the direct polarimetric reading, as a rule, gives the percentage of sucrose accurately enough for practical purposes.

kept constant for an additional 5 mins., when it is rapidly cooled and polarised in a water-jacketed tube, 2 dms. in length, at a known temperature. When the polarimetric observation is made at 20°C., and the reading is multiplied by 2 to raise it to that of a normal solution, the value obtained is −32·66 sugar divisions.

The formula including the correction for temperature when the observation is made at a temperature other than 20°C., is—

$$S=\frac{100K}{142{\cdot}66-0{\cdot}5t}$$

The temperature correction may also be made by Hammerschmidt's formula—

$$I_{20}=I_t+0{\cdot}0038K(20-t),$$

in which I_{20} is the reading of the inverted solution in a 2-dm. tube at 20°C., multiplied by 2, I_t the same at the temperature of observation, and K the difference between the polarisations of the direct and inverted solutions at normal concentration.

If, instead of the half-normal weight in 100 c.c., a solution of a different concentration is employed, the inversion constant varies. Table XI. gives the inversion constants for solutions containing 1–20 grms. of sugar in 100 c.c. The values under I′ are calculated by the formula—

$$I'=-\left(31{\cdot}84+\frac{i}{20}\right),$$

in which i is the polarimetric reading of the inverted solution in a 200 mm. tube, I being the same multiplied by two.

Table XI.

Sugar, grms. in 100 c. c.	I.	I′.	Sugar, grms. in 100 c.c.	I.	I′.
1	31·85	31·90	11	32·52	32·53
2	31·91	31·96	12	32·59	32·60
3	31·98	32·03	13	32·66	32·66
4	32·05	32·09	14	32·73	32·73
5	32·12	32·15	15	32·79	32·79
6	32·18	32·21	16	32·86	32·85
7	32·25	32·28	17	32·93	32·92
8	32·32	32·34	18	33·00	32·98
9	32·39	32·40	19	33·06	33·04
10	32·46	32·46	20	33·13	33·11

The corrections for both temperature and concentration are included in the formula—

$$S=\frac{P-(-I)}{141{\cdot}84+\frac{i}{20}-\frac{t}{2}}$$

P = the direct polarisation.

I = the observed polarisation of the inverted solution corrected proportionately to a normal solution.

P−(−I) = K = the observed Clerget constant at $t°$; i = the observed polarisation of the inverted solution in a 200-mm. tube without any correction.

The writer has confirmed the accuracy of these results (J. Soc. Chem. Ind. 17, 110) as Table XII. shows.

Table XII.

No. of experiment.	C=Grms. per 100 c.c.	I_t. Found.	$I_{20°}$. Calculated from I_t.	$I_{20°}$ (from the above table).	Difference between columns 4 and 5.
1	2·0	$I_{16}=-33{\cdot}92$	−31·92	−31·91	+0·01
2	3·0	$I_{17}=-33{\cdot}05$	−31·55	−31·98	−0·43
3	5·0	$I_{16{\cdot}5}=-33{\cdot}92$	−32·17	−32·12	+0·05
4	7·0	$I_{17}=-33{\cdot}90$	−32·40	−32·25	+0·15
5	10·0	$I_{17}=-33{\cdot}90$	−32·40	−32·46	−0·06
6	13·024	$I_{17}=-34{\cdot}10$	−32·54	−32·66	−0·12
7	13·024	$I_{17{\cdot}5}=-33{\cdot}80$	−32·53	−32·66	−0·13
8	13·024	$I_{16{\cdot}6}=-34{\cdot}20$	−32·47	−32·66	−0·19
9	13·024	$I_{16{\cdot}5}=-34{\cdot}50$	−32·72	−32·66	+0·06
10	13·024	$I_{16{\cdot}5}=-34{\cdot}28$	−32·65	−32·66	−0·01
11	13·024	$I_{19{\cdot}6}=-32{\cdot}60$	−32·40	−32·66	−0·26
12	13·024	$I_{19{\cdot}6}=-32{\cdot}88$	−32·68	−32·66	+0·02
13	13·024	$I_{20}=-32{\cdot}44$	−32·44	−32·66	−0·22
14	13·024	$I_{19{\cdot}4}=-32{\cdot}92$	−32·61	−32·66	−0·05
15	13·024	$I_{19{\cdot}8}=-32{\cdot}72$	−32·62	−32·66	−0·04
16	13·024	$I_{19{\cdot}6}=-32{\cdot}92$	−32·72	−32·66	+0·06

The principal factors which affect the accuracy of the Clerget method in raw products are the following. The volume occupied by the precipitate produced by basic lead acetate; the precipitation of lævulose, and to some extent of dextrose, by basic lead acetate; the effect on the rotation of sugars and of certain amino compounds owing to the presence of hydrochloric acid; and the effect (in the case of the most impure products) of the alkali of the basic lead acetate on the rotatory power of lævulose and of certain amino compounds which they contain.[1]

Eynon (Seventh Inter. Cong. App. Chem. 1909, Sect. V. p. 193) found that in the case of Jaggery sugar and cane molasses, the influence caused by the volume of the lead precipitate was small but more than that due to the influence of

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[1] Andrlik and Stanek have shown (Zeitsch. Zucker-ind. Böhmen, 31, 417), that a 1 p.c. solution of glutaminic acid gave a polarimetric reading of 1·45 Ventzke in presence of basic lead acetate, 0·35 V. in water alone, and 1·77 V. in dilute hydrochloric acid.

the lead left in solution on the rotation of sucrose. Incidentally Eynon's results confirm those of Prinsen-Geerligs (Internat. Sugar J. 10, 500; 11, 276), that lævulose is partially precipitated (and also dextrose, but to a lesser extent) by basic lead acetate.

It is well known that the speed of hydrolysis of sucrose by acids varies with the concentration and nature of the acid employed. Strong acids such as hydrochloric acid, which, according to the ionic theory, exist in solution for the most part dissociated into their ions, hydrolyse much more sucrose in a given time, other things being equal, than do the weaker organic acids.

The dark after-products which are met with in the sugar industry, contain, besides sugar, other organic matters, consisting to some extent—in all probability for the most part—of the salts of organic acids. At all events, a sufficiency of these salts is present to react with the hydrochloric acid added in carrying out Clerget's process, and to replace it partially by much weaker organic acids. The matter is not improved when the solution under investigation is previously clarified, as it usually is, with basic lead acetate, for here the hydrochloric acid is to some extent neutralised by the alkalinity of the basic lead acetate, besides which it is partially replaced by the comparatively weak acetic acid, and there is some danger that the inversion of the sucrose may not have reached completion in the prescribed time. To obviate the presence of an organic acid, it has been proposed by Herles (*see* p. 240) to use a solution of lead nitrate in conjunction with one of sodium hydroxide as clarifying agent. The experiments of Herzfeld and others have shown, however, that the rotatory power of sucrose is diminished by the employment of this clarifying agent.

There is, however, another objection to the use of Clerget's method, as it is at present carried out, for the estimation of sucrose in products containing much 'other organic matter.' Although the presence of a great many definite substances has been demonstrated in the juice of both sugar cane and beetroot, the nature of this organic matter in a given sample of sugar or molasses cannot be determined. It is, however, well known that these substances are to some extent optically active, and experience shows that even after clarification with basic lead acetate some optically active substances besides sugar remain in solution.

Clerget's method presupposes that no other constituent of the sample than the sucrose suffers any change in optical activity by the treatment adopted. But since the agent employed—acid—is a general hydrolyst, we can be by no means certain that this is the case.

It is obvious that if, instead of employing a general hydrolyst such as an acid, we made use of one which would act selectively on sucrose only, the accuracy of the method would be considerably enhanced. Such a hydrolyst is the invertase of yeast, which hydrolyses, or to use the more familiar term, inverts sucrose and other substances having a similar configuration.

O'Sullivan and Thompson (Chem. Soc. Trans. 59, 46) showed that invertase of yeast might be used as hydrolytic agent in the estimation of sucrose; and Ling and Baker (J. Soc. Chem. Ind. 17, 111) proposed a modification of Clerget's method in which the hydrolysis of the sucrose was effected by heating a slightly acidified (with acetic acid) half-normal solution with 0·5 grm. of fresh-pressed yeast for 5 hours at 55°C. Working with pure sucrose in which alumina cream was the sole clarifying agent employed, the Clerget value $I_{20} = -32·56$ was obtained. With dark-coloured products defecation with basic lead acetate had to be resorted to, and this was added after the completion of hydrolysis. The method could not, therefore, give accurate results under these circumstances, for, as already observed, basic lead acetate precipitates certain reducing sugars, notably lævulose.

A method of overcoming this difficulty has been worked out by Ogilvie (J. Soc. Chem. Ind. 30, 62) by removing the lead in solution by means of sulphurous acid prior to hydrolysis. Ogilvie's method is as follows:—

Four times the normal sugar weight of the sample is transferred to a 200 c.c. flask, defecated with the minimum amount of basic lead acetate solution (sp.gr. 1·26), a little alumina cream added, and the liquid made up to the mark at standard temperature, well shaken and filtered. 100 c.c. of the filtrate are measured accurately into a small beaker, sulphur dioxide passed in from a syphon of the liquefied gas till a faint smell is perceptible (the indication that all the lead is precipitated), the liquid is then transferred to a 200 c.c. flask, made up to the mark, and well mixed. Sufficient calcium carbonate (dried) in fine powder to neutralise the excess of acidity, and a little recently ignited kieselguhr are added, after which the solution is filtered. In this way a normal solution is obtained which is sufficiently clarified to give a distinct polarimetric reading, is free from lead and excess of acidity, and is therefore well suited for the invertase inversion.

The method of hydrolysis is as follows: 50 c.c. of the molasses solution, prepared in the manner just described, contained in a 100 c.c. flask, are raised in a constant temperature bath to 50°–55°C. and 0·5 grm. of washed brewery yeast (top-fermentation) and 2 drops of acetic acid are added, the temperature being maintained as near 55°C. as possible for 4½–5 hours. At the end of this time the liquid is cooled, alumina cream or a little kieselguhr added to assist filtration, and the solution is made up to the mark at standard temperature. The clear filtrate is then polarised in a water-jacketed tube (*see* Fig. 7) at 20°C., the temperature being determined by a thermometer reading to 0·1°C.

The value obtained by Ogilvie when working with pure sucrose was $I_{20} = -31·6$, a value which, it will be observed, differs from that obtained by Ling and Baker.

A preparation of invertase may also be used for the hydrolysis. O'Sullivan and Thompson (Chem. Soc. Trans. 57, 834) prepared invertase by allowing washed yeast to remain aside in a jar until it had liquefied. Fischer (Ber. 27, 2985) found that the autolysis of the yeast might be expedited by the addition of chloroform. Hudson (J. Ind. Eng. Chem. 2, 143) has proposed the following method of preparing a solution of invertase based on these observations.

'Break up 5 lbs. of pressed yeast, which may be either baker's or brewer's yeast, add 30 c.c of chloroform to it in a closed flask, and allow it to stand at room temperature (20°C.) overnight. By the morning, the solid mass will have become liquid and it should then be filtered through filter paper, allowing several hours for draining. To the filtrate add neutral lead acetate until no further precipitate forms and again filter. Precipitate the excess of lead from the filtrate with potassium oxalate and filter. To this filtrate add 25 c.c. of toluene and dialyse the mixture in a pig's bladder for 2 or 3 days against running tap water. The dialysed solution is colourless, perfectly clear after filtration, neutral to litmus, has a solid content of about one-half of one p.c., an ash content of a few hundredths of one p.c., will keep indefinitely in an ice box if a little toluene is kept on its surface to prevent the growth of micro-organisms, and is exceedingly active in inverting cane sugar. The invertase solution does not reduce Fehling's solution.'

The invertase or yeast process takes up a considerably longer period of time than the acid hydrolysis process, but it must be remembered that it necessitates no more personal attention. However, the writer does not consider that sufficient work has yet been carried out with the method or a sufficient number of low-grade products of the sugar industry examined by it, to render it of general applicability in technological work (*cf.* below). The majority of sugar technologists have been somewhat reluctant to carry out investigations on this enzyme method, and have always shown a preference for the acid method, and numerous attempts have been made to remove the errors inherent to it when dark after-products are being dealt with. Neutralisation of the free hydrochloric acid in the inverted solution by sodium hydroxide, as pointed out by Browne (*l.c.*, p. 271), removes the influence of the acidity, but introduces a new disturbing factor, namely sodium chloride.

Pellet in 1897 (Bull. Assoc. Chim. Sucr. Dist. 15, 524) proposed to remove the lead in the direct polarisation liquid by sulphurous acid in slight excess, whilst Andrlik and Stanek in 1906 (Zeits. Zuckerind. Böhmen, 31, 417) proposed to add to the direct polarisation liquid the same quantity of hydrochloric acid as is present in the inverted solution together with a certain amount of urea or betaine to retard the hydrolysis of the sucrose by the hydrochloric acid. One objection to this method is that quite an appreciable amount of hydrolysis occurs under these conditions even 2 mins. after the preparation of the solution, and a second objection to the method has reference to the effect of the bases employed by Andrlik and Stanek on the rotation of reducing sugars when present. In the case of beetroot molasses which do not contain reducing sugars or at the most only traces, this method appears to give results which agree well with those obtained by the Pellet method (Ogilvie, *l.c.*).

Ogilvie (Internat. Sugar J. 14, 91) has compared the results obtained with invertase and acid hydrolysis respectively in the case of five samples of cane molasses, and arrives at the following conclusions: (1) The percentages of sucrose found by the acid inversion process usually employed when the direct polarisation is taken in alkaline solution are too high.[1] (2) The percentage of sucrose found when using a neutral direct polarisation liquid may likewise be too high. (3) The values found when using an acid direct polarisation liquid are in close agreement with those obtained by the invertase method.

Ogilvie's results with beet and cane molasses are given in Tables XIII. and XIV.

TABLE XIII.—*Beet Molasses.*

Sample	1	2	3	4
Direct alkaline (basic lead acetate) polarisation	48·8	—	48·6	47·0
Direct neutral polarisation	49·2	52·0	49·0	47·6
Direct acid (Andrlik) polarisation	50·4	53·25	50·0	48·4
Direct acid (Pellet) polarisation	50·3	53·3	—	48·3
Invertase inversion polarisation	−14·6	−16·0	−15·0	−14·4
Acid inversion polarisation	−13·2	−14·6	−13·6	−13·8
Clerget value by invertase	48·5	51·7	48·6	47·1
Clerget value by acid, using alkaline direct polarisation	47·0	—	47·1	46·1
Clerget value by acid, using neutral direct polarisation	47·3	50·5	47·4	46·5
Clerget value by acid, using acid (Andrlik) direct polarisation	48·2	51·4	48·2	47·1
Clerget value by acid, using acid (Pellet) direct polarisation	48·1	51·4	—	47·0

In a later paper Ogilvie (*ibid.* 14, 624) modified the Pellet method of removing the lead from the direct polarisation liquid by means of sulphurous acid, and applied it to the estimation of sucrose in beet molasses by the Clerget process. His procedure is as follows: Twice the normal weight is dissolved in water defecated with basic lead acetate and made up to 200 c.c. with water. Fifty cubic centimeters of this solution are transferred to a 100 c.c. flask, saturated with sulphur dioxide, the flask being immersed in cold water meanwhile, and subsequently made up with water to

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[1] Exactly the opposite result was obtained by Ogilvie when working with beet molasses, which, however, as he points out, has a different composition from the cane product. In the former the disturbing factor is the presence of amino acids, whilst in the latter it is the presence of reducing sugars.

TABLE XIV.—*Cane Molasses.*

—	Cuban molasses		Egyptian molasses	Javan molasses	"American syrup"
	No. 1	No. 2			
Ash (sulphated)	6·77	7·34	10·92	10·97	6·05
Reducing sugars	18·71	18·56	11·70	21·98	26·55
1. Alkaline (basic lead acetate) polarisation	32·20	31·40	39·50	34·30	39·70
2. Neutral direct polarisation	30·50	29·90	38·10	33·46	39·65
3. Acid (HCl and urea) polarisation) (Andrlik)	30·50	30·50	38·40	33·38	39·26
4. Acid (SO$_2$) direct polarisation (Pellet)	30·60	30·50	38·30	33·30	39·10
5. Invertase inversion polarisation	−16·40	−15·50	−17·90	−14·08	−11·40
6. Acid inversion (Herzfeld) polarisation	−16·30	−15·40	−18·02	−14·06	−12·28
7. Percentage of sucrose, using invertase as hydrolyst	35·6	34·4	42·4	36·1	38·7
8. Percentage of sucrose, using acid as hydrolyst, and the alkaline direct polarisation	36·7	35·4	43·4	36·6	39·3
9. Percentage of sucrose, using acid as hydrolyst, and the neutral direct polarisation	35·4	34·2	42·4	35·9	39·2
10. Percentage of sucrose, using acid as hydrolyst, and the acid (HCl and urea) direct polarisation (Andrlik)	35·4	34·7	42·6	35·9	38·9
11. Percentage of sucrose, using acid as hydrolyst, and the acid (SO$_2$) direct polarisation (Pellet)	35·5	34·7	42·5	35·8	38·8

100 c.c. and filtered. For the inversion solution 50 c.c. of the defecated normal solution of molasses are transferred to a 100 c.c. flask, 25 c.c. of water added, and 5 c.c. of hydrochloric acid (sp.gr. 1·19), and treated according to Herzfeld's directions (*see* p. 242). Working under these conditions it is shown that the direct polarisation liquid may be kept for 30 mins. without showing any diminution in rotation. This work appears very promising, and further experiments with both beet and cane molasses will be very welcome.

Estimation of sucrose in presence of reducing sugars by a single observation. Lemeland (Ann. Chim. anal. 15, 416) found that when a mixture of sucrose and reducing sugars is heated with hydrogen peroxide, caustic alkali and a little manganese dioxide, the reducing and optical powers of the reducing sugars are annulled, whilst the optical power of the sucrose is unaffected. Jolles (Zeitsch. Nahr. Genussm. 20, 631) suggests destroying the rotatory power of reducing sugars in admixture with sucrose by boiling 2 p.c. solutions of the mixture for 45 mins. with sufficient sodium or potassium hydroxide to make the solution have a decinormal degree of alkalinity. This method was modified by Pellet and Lemeland (Inter. Sugar J. 13, 616). Cross and Taggart (*ibid.* 14, 448) state, however, that none of these modifications gives satisfactory results. They find the following procedure to yield good results. A normal (Ventzke) solution is prepared, and 50 c.c. are transferred to a 100 c.c. flask, 6·3 c.c. of sodium hydroxide solution of 36°Beaumé added and 7·5 c.c. of hydrogen peroxide (100 volume). The mixture is cooled to prevent effervescence, and the flask is immersed in a bath of water at 55°F. for 20 mins., cooled, acidified with acetic acid, made up to the mark, clarified with dry basic lead acetate and the rotatory power of the filtrate determined. The reading in a 4-dm. tube gives the percentage of sucrose in the sample. It is shown that the results agree with those obtained by the Clerget-Herzfeld method; and Cross and Taggart recommend it for syrups and molasses.

Estimation of raffinose in beet products by the Clerget method. The method of procedure is the same as above described, but the results are calculated by Herzfeld's formulæ (Zeits. Ver. Deut. Zuckerind. 40, 194)—

$$S=\frac{0·5124P-(-I)}{0·839} \qquad R=\frac{P-S}{1·85},$$

where S is the percentage of sucrose, P is the direct polarisation of the normal solution, I the polarisation of the inverted solution at normal concentration, and R the percentage of raffinose. The formula presupposes that the readings have been made at 20°C. If not the temperature corrections given above must be applied.

Estimation of sucrose in presence of other sugars by the Clerget method. The writer has found that sucrose may be estimated with a fair degree of accuracy in presence of dextrins, maltodextrins, maltose, lactose, or glucose, or of mixtures of these carbohydrates by the Clerget method. The carbohydrates mentioned are for the most part not much affected by the Clerget inversion method; but work on the subject is greatly needed. For the estimation of lactose in chocolate by the Clerget method Dubois has devised a process (Cir. 66, U.S. Bur. of Chem., p. 15; quoted by Browne, *l.c.*, p. 280).

Reduction methods of estimating sugars. Those sugars which contain within their molecule a free carbonyl group—aldoses and ketoses—are capable of reducing metallic salts in alkaline solution. This is true of alkaline solutions of silver, mercury, and copper salts. In no case, however, does the reduction conform to a definite reaction, so that these reduction methods are all of an empirical character. They must therefore be carried out under standard conditions, otherwise accurate results cannot be obtained. With special reference to cupric salts, the old assumption that one molecule of glucose reduces five molecules of copper oxide has long since been abandoned. Indeed, different sugars under similar conditions reduce different amounts of cupric oxide.

The most important and most widely used of these reduction methods, so far as their quantitative application is concerned, for the estimation of reducing sugars, are those which depend on the reduction of alkaline solutions of cupric salts. Trommer in 1841 (Annalen, 39, 360) was the first to show that grape sugar reduced alkaline copper solutions whilst cane sugar did not, and to suggest a method of estimating the former based on this fact. Barreswil, a few years later (J. Pharm. Chim. [iii.] 6, 301), showed that the addition of an alkali tartrate to a solution of copper sulphate containing also an alkali hydroxide rendered the reagent more stable. It was not, however, until 1848 that the method of estimating sugars by the cupric reduction method was placed on a sound basis by Fehling (Annalen, 72, 106, 75). Fehling's solution, with but slight modifications, is the one most generally employed at the present time.

The first methods of estimating sugars based on their power of reducing alkaline copper solutions were volumetric. Later gravimetric methods were devised. The most recent and widely adopted form of each of these will be considered in what follows.

Volumetric methods. Passing over the earlier methods based on this principle, the first work on the subject to demand attention is that of Soxhlet in 1878 (J. pr. Chem. [ii.] 21, 227). The work of this chemist was of an important character. He was the first to show that Fehling's solution, when kept, underwent autoreduction, and to suggest keeping the copper sulphate and alkaline tartrate solutions separate and mixing them as required for use. He came to the conclusion that the volumetric method was capable of greater accuracy than any gravimetric method which was then known. Soxhlet, however, worked with very strong solutions of reducing sugars, and he employed 100 c.c. of Fehling's solution. He also used an open dish for his titrations, which leads to errors on account of the oxidising action of the air (*cf.* Kjeldahl, Res. Compte rend. Carlsberg, 4). The relative reducing powers of the most commonly occurring reducing sugars, according to Soxhlet, are as follows: Glucose 100, invert sugar 96·2, lævulose 92·4, lactose 70·3, and maltose 61·0. These values have been confirmed by numerous observers, but it has to be remembered that the reducing power of a sugar varies according to the conditions under which it was determined.

The end point in the volumetric method was first of all determined by the disappearance of the blue colour, but obviously this could not be used in the case of dark-coloured products. The use of ferrocyanide as an indicator for the unreduced copper was then suggested. It is applied in the following manner: When it is judged that the titration is nearing the end point a little of the liquid is filtered off, the filtrate acidified with acetic acid, and a *freshly prepared* solution of potassium ferrocyanide added, when, if there be any unreduced cupric salt, the well-known brown precipitate or coloration will be produced. Perhaps the most convenient way of ascertaining the end point on this principle is by means of the filter tube (described in Wiley's Agricultural Analysis, vol. 3, p. 130). It consists of a piece of glass tubing 20–25 cm. in length and 5–7 mm. in diameter. A shoulder is formed on one extremity, and over this is stretched a piece of fine linen which is fastened on by a piece of cotton. The tube is dipped into water containing finely divided asbestos in suspension, and some of this is drawn into the tube by suction at the open end. This forms a layer which will retain the cuprous oxide produced in the Fehling reducing method.

The volumetric method of estimating reducing sugars has within recent years been standardised by Ling and Rendle (Analyst, 30, 183), and Ling and Jones (*ibid.* 33, 160). These chemists performed the titration in an ordinary boiling flask, which, however, had been used by the writer and others many years before the papers cited appeared. The main point which they claim to have established by their work, however, is that of having proved that the volumetric method of estimating sugars is quite as accurate and far more convenient than any form of the gravimetric method.

It may here be mentioned that the composition of the alkaline tartrate solution employed by different chemists varies somewhat, more especially as regards the proportion of sodium hydroxide present. It is well known that the results are largely influenced by the proportion of sodium hydroxide.

The reagent used by the writer and his co-workers is prepared as follows:—

Solution No. 1. Crystallised copper sulphate (69·2 grms.) is dissolved in water and the solution made up to one litre.

Solution No. 2. Crystallised Rochelle salt (346 grms.) is dissolved in hot water and mixed with sodium hydroxide (142 grms.) also dissolved in water. After cooling the mixed solutions are made up to one litre.

Equal volumes of these two solutions are accurately measured out at 15·5°C. or any other standard temperature adopted, and this mixture constitutes the reagent.[1]

The method was standardised for a volume of the mixed solution of 10 c.c., but occasionally it is necessary to vary this volume, and Ling and Jones (*l.c.*) show that assuming the concentration of the sugar solution to be constant, the number of cubic centimetres required for any titration is directly proportional to the volume of copper reagent employed—at all events when this lies between the limits of 5 and 20 c.c.

The indicator employed by the writer and his co-workers is an acid solution of ferrous thiocyanate, which is prepared as follows:—

Ammonium thiocyanate . .	1·5 grms.
Ferrous ammonium sulphate .	1·0 „
Concentrated hydrochloric acid	2·5 c.c.
Water	10·0 „

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[1] The measurement of equal volumes of these solutions at definite temperatures is a most important point, since the coefficient of expansion of each solution is different and differs also from that of water.

The solution prepared even from the purest reagents has invariably a brownish-red colour due to the presence of ferric salt, which latter must therefore be reduced. For this purpose zinc dust has been found to be the most satisfactory reagent, and, as a rule, a mere trace suffices to decolorise the solution.

The method of titration is as follows: The freshly mixed copper reagent (10 c.c.) is accurately measured into a 200 c.c. boiling flask. The reagent, which is not diluted with water, is heated to boiling. The sugar solution, which should be adjusted to such a strength that 20–30 c.c. of it are required to reduce 10 c.c. of Fehling's solution,*is then run into the boiling liquid in small amounts, commencing with 5 c.c. After each addition of sugar solution the mixture is boiled, the liquid being kept rotated. About a dozen drops of the indicator are placed on a porcelain or opal glass slab, and when it is judged that the precipitation of cuprous oxide is complete, a drop of the liquid is withdrawn by a clean glass rod or by a capillary tube, and brought in contact with a drop of the indicator on the slab. The test must be carried out rapidly. It is also essential to perform the titration as rapidly as possible, as an atmosphere of steam is then kept in the neck of the flask and the influence of atmospheric oxygen avoided. At the final point the liquid is boiled for about 10 seconds. As in the ordinary volumetric method, the first titration may only give approximate results, and a second or third will then be necessary to establish the end-point accurately. However, when the operator has gained experience, the first titration is as much to be relied on as succeeding ones, and this point is clearly brought out in the results cited. One titration takes from 2½ to 3 mins.

The copper reagent is standardised against invert sugar as follows: Pure sucrose (0·95 grm.) (*see* p. 235) is dissolved in water (150 c.c.), and boiled with N/2 hydrochloric acid (30 c.c.), the mixture being maintained in ebullition for 1 min., cooled, neutralised by the addition of N/2 sodium hydroxide (30 c.c.), and made up with water to 500 c.c. This solution, which contains 0·2 grm. of invert sugar per 100 c.c. is titrated against 10 c.c. portions of the copper reagent, as above described.

It should here be pointed out that whilst the thiocyanate indicator is by far the most delicate and satisfactory, it cannot be used with commercial products containing iron. With these the ferrocyanide indicator must be employed.

Ling and Jones (*l.c.*) have calculated a table for dextrose, lævulose, invert sugar, and maltose for a range of concentrations such that using 10 c.c. of Fehling's solution the reduction is complete with the addition of 20–43 c.c. of the sugar solution.

TABLE XV.

Volume of solution required by 10 c.c. Fehling's solution	Dextrose		Lævulose		Invert sugar		Maltose	
	D Dextrose in 100 c.c. of solution	D′ Fehling's solution equivalent to 1 grm. dextrose	L Lævulose in 100 c.c. of solution	L′ Fehling's solution equivalent to 1 grm. lævulose	I Invert sugar in 100 c.c. of solution	I′ Fehling's solution equivalent to 1 grm. invert sugar	M Maltose in 100 c.c. of solution	M′ Fehling's solution equivalent to 1 grm. maltose
c.c.	grm.	c.c.	grm.	c.c.	grm.	c.c.	grm.	c.c.
20	0·2427	206·0	—	—	—	—	—	—
21	0·2332	205·1	—	—	0·2412	197·5	0·3888	122·5
22	0·2226	204·2	0·2411	188·5	0·2311	196·8	0·3711	
23	0·2138	203·4	0·2312	188·0	0·2218	196·0	0·3550	
24	0·2056	202·6	0·2222	187·5	0·2132	195·5	0·3402	
25	0·1981	201·9	0·2138	187·1	0·2052	194·9	0·3266	
26	0·1911	201·3	0·2060	186·7	0·1980	194·3	0·3140	
27	0·1846	200·7	0·1988	186·3	0·1910	193·9	0·3023	
28	0·1784	200·1	0·1921	186·0	0·1846	193·4	0·2915	
29	0·1728	199·6	0·1857	185·6	0·1787	193·0	0·2815	
30	0·1675	199·1	0·1798	185·4	0·1731	192·5	0·2721	A constant
31	0·1625	198·6	0·1743	185·1	0·1678	192·2	0·2633	
32	0·1577	198·2	0·1691	184·8	0·1629	191·8	0·2551	
33	0·1532	197·8	0·1642	184·6	0·1583	191·5	0·2474	
34	0·1490	197·4	0·1596	184·3	0·1539	191·2	0·2401	
35	0·1450	197·0	0·1552	184·1	0·1497	190·9	0·2332	
36	0·1412	196·7	0·1511	183·9	0·1458	190·6	0·2268	
37	0·1377	196·4	0·1472	183·6	0·1421	190·3	0·2206	
38	0·1343	196·0	0·1435	183·4	0·1385	190·1	0·2148	
39	0·1310	195·8	0·1399	183·3	0·1349	189·8	0·2093	
40	0·1279	195·5	0·1366	183·1	0·1319	189·6	0·2041	122·5
41	—	—	0·1334	182·9	0·1288	189·4	—	
42	—	—	0·1298	182·8	0·1259	189·2	—	—
43	—	—	0·1274	182·6	—	—	—	—

The manner of using the table is best explained by an illustration. Suppose a solution of pure lævulose is being examined, and that 25·0 c.c. of it are required to reduce 10 c.c. of Fehling's solution. Opposite 25 in the first column is found 0·2138 in column L; the percentage of lævulose in the solution titrated is thus given direct. If 25·2 c.c., or other quantity not a whole number, is required to reduce 10 c.c. of Fehling's solution, the percentage of lævulose can be easily found by interpolation between the numbers in column L.

The table gives the number of cubic centimetres of Fehling's solution equivalent to 1 grm. of the particular sugar at each concentration. These numbers, given in columns D′, L′, I′, and M′, have another purpose—namely, the separate determination of two reducing sugars in a mixture, by a modification of the method of Morris (J. Inst. Brewing, 4, 162), which depends on the reducing power and the reading in the half-shadow Ventzke polarimeter when observed in a 2-dm. tube. The application of the table for this purpose is described on pp. 259, 261.

Estimation of invert sugar in presence of cane sugar. It is well known that sucrose, although by constitution a non-reducing sugar, does reduce Fehling's solution to some extent when boiled therewith, and that in mixtures of sucrose and invert sugar, such as raw sugars, cane syrups and cane molasses, it is necessary to apply a correction when estimating the invert sugar in these by any method involving cupric reduction. Ling and Rendle (*ibid.* 33, 170) have determined the corrections to be applied for the influence of sucrose when their method is used for the analysis of mixtures such as those referred to.

In the following table:—

Column A gives the amounts in grams of sucrose present in 100 c.c. of the sugar solutions.

Column B gives the percentages of sucrose present expressed on the total sugars.

Column C gives the percentages of invert sugar present expressed on the total sugars.

Column D gives the number of cubic centimetres of sugar solution required to reduce 10 c.c. of Fehling's solution.

Column E gives the percentages of invert sugar on the total sugars found by direct experiment.

Column F gives the differences between the values shown in columns C and E.

TABLE XVI.

Each solution contained, in addition to the sucrose shown under column A, 0·2 gram of invert sugar per 100 c.c.

A	B	C	D	E	F
0·01	4·8	95·2	25·60	95·30	0·10
0·03	13·0	87·0	25·60	87·10	0·10
0·05	20·0	80·0	25·60	80·10	0·10
0·10	33·3	66·7	25·55	66·90	0·20
0·20	50·0	50·0	25·45	50·40	0·40
0·30	60·0	40·0	25·40	40·40	0·40
0·40	66·6	33·4	25·35	33·80	0·40
0·50	71·4	38·6	25·30	29·00	0·40
0·60	75·0	25·0	25·20	25·40	0·40
0·70	77·7	22·3	25·15	22·70	0·40
0·80	80·0	20·0	25·10	20·40	0·40
1·25	86·2	13·8	25·05	14·10	0·30
1·50	88·2	11·8	24·95	12·10	0·30
1·75	89·7	10·3	24·85	10·60	0·30
1·75	89·7	10·3	24·80	10·60	0·30
2·00	90·9	9·1	24·70	9·45	0·35
2·00	90·9	9·1	24·80	9·41	0·31
2·50	92·5	7·5	24·80	7·76	0·26
3·00	93·8	6·2	24·70	6·44	0·24
5·00	96·1	3·9	24·20	4·05	0·15
7·00	97·2	2·8	23·60	3·04	0·24
10·00	98·0	2·0	22·95	2·23	0·23
20·00	99·0	1·0	22·40	1·14	0·14
25·00	99·2	0·8	22·25	0·92	0·12
30·00	99·3	0·7	22·25	0·80	0·10

In addition to these results Ling and Rendle (*l.c.*) also carried out determinations for mixtures of sucrose and invert sugar when the concentration of the latter sugar was 0·15 grm. and 0·25 grm. per 100 c.c. respectively.

An examination of the table shows that the influence of sucrose is practically negligible until the proportion to the total sugars (sucrose and invert sugar) amounts to 30 p.c. (*see* column B), at which point the invert sugar is overestimated by 0·2 p.c. This influence of sucrose increases progressively until the proportion, expressed on the total sugars, 99·3 p.c. is reached, beyond which it has not been determined. At this point the invert sugar is overestimated to the extent of about 15 p.c. It must be remembered, however, that the magnitudes representing the percentages of invert sugar decrease as those representing the percentages of sucrose increase, and it will be seen that the correction to be applied (column F) is in concrete numbers the greatest when the percentage of sucrose on the total sugars is between 50 and 80. In the case of a mixture of equal parts of sucrose and invert sugar, the latter would be returned if no correction were applied as 50·4 p.c. instead of 50·0 p.c., whilst in the case of a mixture of 99 parts of sucrose and 1 part of invert sugar, the latter would be returned if no correction were applied as 1·14 p.c. instead of 1 p.c. The writer is in the habit in practice of deducting the values shown in column F of the table from the values determined by direct titration of the mixture of sugars. For this purpose, however, it is necessary to know the percentage of sucrose, not calculated on the sample, but on the total sugars (sucrose and invert sugar) in the sample. This can be determined either by the Clerget method or by the method of double titration before and after hydrolysis with hydrochloric acid, applying the formula $S=\frac{(95I'-I)}{100}$, in which S is the approximate percentage of sucrose, I is the apparent percentage of invert sugar—*i.e.* the value obtained by direct titration—and I′ is the percentage of invert sugar obtained by titration of the sample after complete hydrolysis.

The approximate value given in column F is subtracted from the value of I and added to the value of S, the respective results giving the corrected percentages of invert sugar and of sucrose. In order to express these on the sample, each of the values is multiplied by $S+I/100$. To be exact, the value added to the approximate percentage of sucrose, S, should be diminished by 5 p.c.; but the accuracy of the method does not warrant this refinement, seeing that the corrections to be applied are values of comparatively small magnitude.

In the early days when the end point in the titration method was determined by the disappearance of the blue colour, a difficulty was experienced in titrating dark coloured physiological liquids with the ordinary Fehling's solution. Nor can the ferrocyanide indicator be used with these liquids, since they invariably contain amino compounds, which partially dissolve the precipitated cuprous oxide. It is true that cuprous solutions do not give a coloration with ferrocyanide, but it is necessary to acidify with acetic acid before this indicator can be applied, and acidified solutions of cuprous salts when exposed to air rapidly oxidise to the cupric state. The writer has not found the same difficulty with his ferrous thiocyanate indicator, which, in the absence of iron, may be used for the titration of physiological solutions.

To obviate the difficulties referred to in the preceding paragraph, F. W. Pavy, in 1879 (Proc. Roy. Soc. 28, 260), proposed to employ a copper solution containing sufficient ammonia to keep the reduced cuprous oxide in solution. Since the disturbing influence of the precipitated cuprous oxide on the colour is thus prevented as well as that due to the presence of amino compounds, it is possible, in absence of air, to titrate moderately dark coloured physiological liquids, using Pavy's solution, with sufficient accuracy. The method has been applied specially for the estimation of dextrose in urine. It should be added, however, that the colour of many physiological liquids is sufficient to render accuracy impossible with Pavy's method.

Pavy's solution is prepared as follows: crystallised copper sulphate (34·65 grms.), Rochelle salt (170 grms.) and potassium hydroxide (170 grms.) are dissolved in water and made up to one litre. The copper and alkaline tartrate solutions are preferably made up separately and equal volumes mixed as required (see p. 247). To 120 c.c. of the mixed solutions is added ammonia of sp.gr. 0·880 (300 c.c.), and the liquid is diluted to one litre. Working under the conditions to be described, 20 c.c. of this solution are reduced by 0·01 grm. of glucose. If other sugars are to be estimated, the titre of the solution must be established for each of these.

The titration is performed in the following manner. A round-bottomed flask of 150 c.c. capacity is provided with a doubly-bored rubber stopper. Through one opening in the stopper the delivery end of the burette passes and through the other a glass tube bent twice at right angles, the latter being intended for the escape of the steam and to prevent the access of air. Forty cubic centimetres of the ammoniacal copper solution are introduced into the flask and after inserting the stopper the solution is raised slowly to boiling. The assay liquid is then added at the rate of 60 to 100 drops per minute, ebullition being maintained meanwhile (a special pinch cock was employed by Pavy). When the blue colour is nearly discharged, the assay liquid is added drop by drop until no more blue can be discerned. A sheet of white paper or a plate of opal glass placed behind the flask assists in determining the end point more accurately.

For the estimation of reducing sugars in small quantities, Bang (Biochem. Zeitsch. 1906, 2, 271) makes use of the principle that cuprous oxide separates as cuprous thiocyanate from a solution of cupric sulphate containing alkali carbonates (not hydroxides) and potassium thiocyanate. The unreduced copper salt is then also precipitated as cuprous thiocyanate by titration with a standard solution of hydroxylamine in the presence of an excess of potassium thiocyanate. The method is said to be accurate and to be adapted for the estimation of sugar in urine. The following solutions are employed.

Copper solution. Potassium carbonate (250 grms.), potassium bicarbonate (50 grms.) and potassium thiocyanate (211 grms.) are dissolved by warming in water (600 c.c.). To the cooled liquid is slowly added a solution of crystallised copper sulphate (12·5 grms.) in about 75 c.c. of water. The mixture is then made up to a litre.

Hydroxylamine solution. Hydroxylamine sulphate (6·55 grms.) and potassium thiocyanate (200 grms.), are dissolved in water and the solution made up to two litres.

In carrying out the titration the sugar solution (10 c.c.), which should not contain more than 60 mgrms. of dextrose, is measured into a 200 c.c. flask and 50 c.c. of the copper solution added. The mixture is heated to boiling and maintained in ebullition for exactly 3 mins. The liquid is then cooled and the hydroxylamine solution run in from a burette until the blue colour is completely discharged. The results are calculated by the following table.

TABLE XVII.

Hydroxylamine	Glucose	Hydroxylamine	Glucose
c.c.	mgs.	c.c.	mgs.
43·85	5	17·75	33
42·75	6	16·95	34
41·65	7	16·15	35
40·60	8	15·35	36
39·50	9	14·60	37
38·40	10	13·80	38
37·40	11	13·05	39
36·40	12	12·30	40
35·40	13	11·50	41
34·40	14	10·90	42
33·40	15	10·20	43
32·45	16	9·50	44
31·50	17	8·80	45
30·55	18	8·20	46
29·60	19	7·65	47
28·65	20	7·05	48
27·75	21	6·50	49
26·85	22	5·90	50
26·00	23	5·35	51
25·10	24	4·75	52
24·20	25	4·20	53
23·40	26	3·60	54
22·60	27	3·05	55
21·75	28	2·60	56
21·00	29	2·15	57
20·15	30	1·65	58
19·35	31	1·20	59
18·55	32	0·75	60

Methods have been devised in which the cuprous oxide reduced under standard conditions by sugars is collected on a filter and subsequently dissolved and the copper titrated by one of the well-known methods. These will be referred to under gravimetric methods (see p. 252).

Gravimetric methods. The preference shown by many workers for gravimetric methods as compared with volumetric methods is based on the fact that weighings can be conducted with a greater degree of delicacy than can titrations. But whilst this is true, it by no means follows that the former are less accurate than the latter. In the first place, the empirical character of methods depending on the reduction of cupric solutions by sugars must be borne in mind, for, even with solutions of pure sugars the variations of conditions in even a slight degree causes considerable alterations in the results, so that increased delicacy does not of necessity synchronise with increased accuracy. Moreover, in the case of commercial products there are other factors which tend to vitiate the accuracy of the gravimetric methods. Thus these products contain certain salts of the alkali earth metals and nitrogenous matters. The former are liable to be precipitated with the cuprous oxide, whilst the latter are capable of dissolving some of the cuprous oxide. Errors of the former kind may be avoided by dissolving the washed cuprous oxide and estimating the copper volumetrically; but it is impossible to eliminate the errors due to the solvent action of the nitrogenous matters on the cuprous oxide. Neither of these factors affect the accuracy of methods of direct titration. Concordance of results in gravimetric methods does not, therefore, of necessity indicate accuracy.

It is impossible in this article to deal exhaustively with the numerous methods which have been proposed for the estimation of reducing sugars by weighing the cuprous oxide precipitated under standard conditions. The writer must confine himself to a description in detail of some of those methods which are in most general use. Taking them in their chronological order, the principal investigators to whom we are indebted for our knowledge on this subject are Soxhlet, Allihn, Wein, Meissl, Herzfeld, Lehmann, Kjeldahl, Brown, Morris and Millar, Defren, and Bertrand.

In most of the new methods, workers have started on an entirely new basis from that adopted by those that preceded them, altering not only the composition of the alkaline copper solution but also the mode of carrying out the reduction. Thus some use a larger proportion of alkali, whilst others have departed from the original prescription of Fehling so far as to employ potassium hydroxide instead of sodium hydroxide.[1] It therefore happens that we are in possession of a large number of empirical tables which can only be used under strictly standardised conditions.

In the earlier gravimetric methods the cuprous oxide was collected on a paper filter, and after washing, the precipitate and filter were ignited and the copper weighed as cupric oxide. This method is subject to several errors, *e.g.* the paper in spite of repeated washing retains some of the copper, possibly by adsorption, and as this is by no means a constant quantity it cannot be corrected for; again, it is difficult to burn the precipitate to cupric oxide in a crucible even if, after one burning, it be treated with nitric acid and again ignited. The method has, therefore, now been superseded by one in which the cuprous oxide is collected under diminished pressure in a Soxhlet tube packed with asbestos. The following is a description of a Soxhlet tube. The tube is made of hard glass, and the total length is about 20 cm. The upper portion is a parallel-walled tube, having an internal diameter of about 1·5 cm., and is about 12 cm. long. Below this the tube is constricted to a bore of about 1 mm., and the remaining portion of the tube below the constriction tapers towards the end in order that it may be fitted into the hole of a rubber stopper which fits into the filter flask attached to the pump. The Soxhlet tube is packed with asbestos in the manner to be described. Another method of collecting the cuprous oxide obtained by the reduction of Fehling's solution is by the use of a Gooch crucible, which is also packed with asbestos.

The asbestos used for this purpose must be subjected to treatment with acid and alkali, otherwise it loses weight when the alkaline copper solution is filtered through it. The following method recommended for this purpose by Munson and Walker (J. Amer. Chem. Soc. 28, 666) may be used. The asbestos, which should be of the amphibole variety, is digested with 1 : 3 hydrochloric acid for 2 to 3 days, after which it is washed free from acid and digested for a similar period with soda solution,[1] following which it is treated with hot Fehling's solution. The asbestos is now washed free from alkali and finally digested with nitric acid for several hours, after which it is washed free from acid and suspended in water for use. It is best kept suspended in water in a wide-mouthed stoppered bottle.

To prepare a Soxhlet tube for use, a small amount of the prepared asbestos suspended in water is introduced into the tube which is in connection with the filter pump, just as it would be when being used for the collection of the copper precipitate. The tube thus charged with asbestos is then dried in the water oven and cooled in the desiccator when it is ready for use.

A Soxhlet tube, prepared as just described, is tared, and the cuprous oxide having been collected in it and washed with hot water, principally by decantation, the tube is dried in the water oven. The drying may be facilitated by washing finally with alcohol and ether before placing in the oven. The most commonly adopted plan is to reduce the cuprous oxide to metallic copper before weighing. This is done by connecting the wider end of the tube with a hydrogen generating apparatus and igniting that portion of the tube containing the cuprous oxide by a Bunsen flame, a current of hydrogen being passed through the tube meanwhile. Prior to this, however, in the most exact work, especially with commercial products, it is advisable to ignite in a current of oxygen in order to remove any organic matter that may have been precipitated with the cuprous oxide. Some chemists weigh the precipitate as cupric oxide after ignition in current of oxygen. It has also been proposed to weigh the precipitate after merely drying, and in the case of sugar solutions not containing other organic matters this appears not to be attended with any error (*cf.* O'Sullivan and Stern, Chem. Soc. Trans. 69, 1691). Ling and Davis (J. Inst. Brewing, 8, 477), employing a Gooch crucible, weighed the copper precipitate as cuprous oxide, that is to say, they merely dried it after collection, and their results show that with pure solutions this procedure is

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[1] In this connection it should be pointed out that Glendinning (Chem. Soc. Trans. 67, 999) has shown that, other things being equal, considerably higher results are obtained when potassium hydroxide is substituted for the sodium compound.

[1] The writer uses a 50 p.c. solution of sodium hydroxide for this purpose.

justifiable on the score of accuracy. Whichever method is adopted, the Soxhlet tube or Gooch crucible, after being weighed with the copper should be treated with nitric acid to dissolve the copper, and the asbestos thoroughly washed. After drying, the tare of the tube should be the same as it was at the commencement of the experiment.

The washed cuprous oxide collected on a Soxhlet tube or Gooch crucible may also be dissolved in nitric acid or a mixture of that acid and sulphuric acid, the copper deposited electrolytically and weighed as metal (see Bull. 107 [revised], U.S. Bur. of Chem., p. 49). Peters has devised a rapid electrolytic method of estimating copper (J. Amer. Chem. Soc. 34, 426). Another electrolytic method is that of Sand described in the Report of the British Association for the Advancement of Science, 1910.

The washed cuprous oxide may be dissolved in sulphuric acid and the solution titrated with permanganate. Many methods have been proposed for this purpose (Neitzel, Jahresber. Zuckerfabrik. 1893, 104; Kalmann, Osterr. Zeit. Zuckerind., 25, 43; Thorne and Jeffers, Analyst, 30, 188).[1] The usual way in which the method is carried out is to transfer the cuprous oxide and asbestos wad to 50 c.c. of a solution containing an excess of iron alum, acidified with sulphuric acid. The solution is then titrated with N/20 permanganate (*cf.* also Bull. 107 U.S. Bur. of Chem., *l.c.*). Another method of estimating the cuprous oxide reduced by sugar solutions is based on the well-known principle of liberation of iodine by cupric salts and titration of the iodine with thiosulphate. The washed precipitate is dissolved in nitric acid, and the solution boiled until the red fumes are expelled. It is then made alkaline with ammonia and acidified with acetic acid. An excess of potassium iodide is then added and the liberated iodine is titrated in the well-known manner (Low, J. Amer. Chem. Soc. 24, 1082; Kendall, *ibid.* 23, 1947; Peters, *ibid.* 34, 422). This iodometric method gives low results as compared with those obtained by the gravimetric method (Sherwood and Wiley, Bull. 105, U.S. Bur. of Chem., p. 120).

Allihn's method. One of the best known and most widely used methods of estimating dextrose gravimetrically by the cupric reduction method is that of Allihn (J. prakt. Chem. [ii.], 22, 46), but it has not been applied to any other sugar. The copper reagent used has the following composition:—

Solution I. Crystallised copper sulphate (34·6 grms.) is dissolved in water and the solution made up to 500 c.c.

Solution II. Rochelle salt (173 grms.) and potassium hydroxide (125 grms.) are dissolved in water and the solution made up to 500 c.c.

Equal volumes of 30 c.c. of each of the two solutions are measured out into a beaker and diluted with 60 c.c. of water. A volume of 25 c.c. of a standard solution of the sample to be examined, which must not contain more than 0·25 grm. of dextrose, is added and the solution is raised to the boiling-point, ebullition being continued for 2 mins. It is important in this and in all other estimations of the kind that the beaker should be covered with a clock glass during the ebullition.[1] The cuprous oxide is collected at once in a Soxhlet tube, washed, dried, and reduced in a current of hydrogen in the manner already described. In the following table, which is an abridged form of that given for the Allihn method by the A. O. A. C. (Bull. 107 [revised], U.S. Bur. of Chem., p. 49), the weight of copper and of cuprous oxide corresponding to different weights of dextrose are given.

TABLE XVIII.—*Allihn's Table for Estimating Glucose.*

Copper (Cu)	Cuprous oxide (Cu_2O)	Glucose	Copper (Cu)	Cuprous oxide (Cu_2O)	Glucose
mgs.	mgs.	mgs.	mgs.	mgs.	mgs.
11	12·4	6·6	241	271·3	124·4
16	18·0	9·0	246	277·0	127·1
21	23·6	11·5	251	282·6	129·7
26	29·3	14·0	256	288·2	132·4
31	34·9	16·5	261	293·8	135·1
36	40·5	18·9	266	299·5	137·8
41	46·2	21·4	271	305·1	140·6
46	51·8	23·9	276	310·7	143·3
51	57·4	26·4	281	316·4	146·1
56	63·0	28·8	286	322·0	148·8
61	68·7	31·3	291	327·4	151·6
66	74·3	33·3	296	333·3	154·3
71	79·9	36·3	301	338·9	157·1
76	85·6	38·8	306	344·5	159·8
81	91·2	41·3	311	350·1	162·6
86	96·8	43·9	316	355·8	165·3
91	102·4	46·4	321	361·4	168·1
96	108·1	48·9	326	367·0	170·9
101	113·7	51·4	331	372·7	173·7
106	119·3	54·0	336	378·3	176·5
111	125·0	56·5	341	383·9	179·3
116	130·6	59·1	346	389·6	182·1
121	136·2	61·6	351	395·2	184·9
126	141·9	64·2	356	400·8	187·7
131	147·5	66·7	361	406·4	190·6
136	153·1	69·3	366	412·1	193·4
141	158·7	71·8	371	417·7	196·3
146	164·4	74·4	376	423·3	199·1
151	170·0	77·0	381	429·0	202·0
156	175·6	79·6	386	434·6	204·8
161	181·3	82·2	391	440·2	207·7
166	186·9	84·8	396	445·9	210·6
171	192·5	87·4	401	451·5	213·5
176	198·1	90·0	406	457·1	216·4
181	203·8	92·6	411	462·7	219·3
186	209·4	95·2	416	468·4	222·2
191	215·0	97·8	421	474·0	225·1
196	220·7	100·5	426	479·6	228·0
201	226·3	103·1	431	485·3	231·0
206	231·9	105·8	436	490·9	233·9
211	237·6	108·4	441	496·5	236·9
216	243·2	111·1	446	502·1	239·8
221	248·7	113·7	451	507·8	242·8
226	254·4	116·4	456	513·4	245·7
231	260·1	119·0	461	519·0	248·7
236	265·7	121·7			

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[1] Also private communication to the writer from Dr. L. T. Thorne.

[1] The reason that it is necessary to cover the beaker with a clock glass has already been alluded to as well as the observations of Kjeldahl (*l.c.*) on this point. Kjeldahl went even further and suggested carrying out the reduction in a flask immersed in a bath of boiling water, a current of hydrogen being passed through the solution during the ebullition. Kjeldahl's

Meissl's method for the estimation of invert sugar (Zeit. Ver. Deut. Zuckerind, 29, 1050) is carried out in the same manner as Allihn's dextrose method, but the copper solution employed was that of Soxhlet, containing 52 grms. per litre of sodium hydroxide. Wein (Tabellen für quantitative Bestimmung der Zuckerarten, 1888) used the same solution for the estimation of maltose and other sugars. The results for maltose calculated by Wein's tables were found to be 5 p.c. too low by Brown, Morris and Millar (Chem. Soc. Trans. 71, 105), and this has been confirmed by Ling and Baker (*ibid.* 509).

Standard gravimetric methods have been devised, each of which is capable of being used for the estimation of several sugars. The first of these which will be described here is that of Brown, Morris and Millar (*l.c.*) for the estimation of dextrose, lævulose, invert sugar and maltose. The method adopted is that of O'Sullivan. The copper reagent employed had the following composition. Crystallised copper sulphate (34·6 grms.), Rochelle salt (173 grms.), sodium hydroxide (65 grms.), and water to one litre.[1]

Fifty cubic centimetres of the copper solution are introduced into a beaker, the surface area of which is 44 sq. cm. The beaker is covered with a clock glass and immersed in a bath of boiling water. When the solution has attained the same temperature as that of the bath, the sugar solution is added and the mixture made up to approximately 100 c.c. with boiling water and heated in the boiling water bath for exactly 12 mins. The amount of sugar employed must be that which will give a weight of cupric oxide lying within the limits of 0·15 to 0·35 grm. The filtration is performed as rapidly as possible through a Soxhlet's tube under reduced pressure, and the cuprous oxide is either oxidised to cupric oxide in a current of oxygen or reduced to copper in a current of hydrogen. The results are calculated by Tables XIX–XXII.

Defren (J. Amer. Chem. Soc. 18, 751) has worked out a method for the estimation of dextrose, maltose and lactose. He employs, like Meissl and Wein (see above), Soxhlet's formula for Fehling's solution, but adopts the O'Sullivan method.

Bertrand (Bull. Soc. chim. [iii.] 35, 1285) has elaborated a method for the estimation of invert sugar, dextrose, galactose, maltose and lactose. His reagent has the following composition:

Solution I. Crystallised copper sulphate (40 grms.) is dissolved in water and made up to one litre.

Solution II. Rochelle salt (150 grms.) and sodium hydroxide (150 grms.) are dissolved in water and made up to one litre.

His method is carried out as follows: A sugar solution (20 c.c.) which should not contain more than 0·1 grm. of reducing sugars is transferred to a 150 c.c. Erlenmeyer flask, and 20 c.c. of each of the two solutions forming the copper reagent added. The mixture is then heated to boiling, and maintained in gentle ebullition for exactly 3 mins. The liquid is then filtered through a Gooch crucible, the precipitate washed as usual and the reduced copper estimated volumetrically by the permanganate method (see p. 252). Table XXIII. is Bertrand's table abridged from the original.

TABLE XIX.—*Dextrose.*

Dextrose mgrms.	Cu weighed grms.	CuO weighed grms.	Cu corresponding to 1 grm. dextrose	CuO corresponding to 1 grm. dextrose
50	0·1030	0·1289	2·060	2·578
55	0·1134	0·1422	2·066	2·585
60	0·1238	0·1552	2·068	2·587
65	0·1342	0·1682	2·069	2·589
70	0·1443	0·1809	2·066	2·585
75	0·1543	0·1935	2·062	2·580
80	0·1644	0·2061	2·059	2·577
85	0·1740	0·2187	2·055	2·572
90	0·1834	0·2299	2·042	2·555
95	0·1930	0·2420	2·036	2·547
100	0·2027	0·2538	2·029	2·538
105	0·2123	0·2662	2·027	2·535
110	0·2218	0·2781	2·021	2·528
115	0·2313	0·2900	2·016	2·522
120	0·2404	0·3014	2·008	2·512
125	0·2496	0·3130	2·002	2·504
130	0·2585	0·3241	1·993	2·493
135	0·2675	0·3354	1·986	2·484
140	0·2762	0·3463	1·977	2·473
145	0·2850	0·3573	1·970	2·464
150	0·2934	0·3673	1·957	2·448
155	0·3020	0·3787	1·953	2·443
160	0·3103	0·3891	1·944	2·432
165	0·3187	0·3996	1·936	2·422
170	0·3268	0·4098	1·926	2·410
175	0·3350	0·4200	1·918	2·400
180	0·3431	0·4302	1·910	2·390
185	0·3508	0·4399	1·900	2·377
190	0·3590	0·4501	1·894	2·369
195	0·3668	0·4599	1·885	2·358
200	0·3745	0·4689	1·874	2·344
205	0·3822	0·4792	1·869	2·338

As already mentioned, numerous other metallic solutions besides that originally devised by Fehling have been used for the detection and estimation of reducing sugars. These will now be dealt with in outline.

Barfoed (Zeitsch. anal. Chem. 12, 27) proposed to use a solution one part of crystallised neutral copper acetate in 15 parts of water. To 200 c.c. of this solution are added 5 c.c. of 38 p.c. acetic acid before use. Barfoed's solution is not reduced to any great extent by the bioses maltose, lactose, &c., but although it has some value in the case of mixture of monoses and bioses, this applies to it for qualitative rather than quantitative purposes.

It has been proposed by Soldaini (Ber. 9, 1126) and also subsequently by another chemist of the same name (Zeits. Ver. Deut. Zuckerind.

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method has been modified by Woy (Zeits. öffentl. Chem. 6, 514; 519). Working with pure sugar solutions there is no doubt that more concordant results can be obtained in this way, but with commercial products, in which this atmospheric oxidation is perhaps one of the least factors which conduce to error, the covering of the beaker with a clock glass is a sufficient precaution to guard against atmospheric oxidation. In the Allihn method the size of the beaker, the kind and height of the flame employed also influence the results. On this account the O'Sullivan method of heating in a boiling water bath as adopted by Kjeldahl, Brown, Morris and Millar (see this page), and others is to be preferred.

[1] The copper culphate solution and the alkaline Rochelle salt solution are, of course, kept separate.

Table XX.—*Lævulose.*

Lævulose mgrms.	Cu weighed grms.	CuO weighed grms.	Cu corresponding to 1 grm. lævulose	CuO corresponding to 1 grm. lævulose
50	0·0923	0·1155	1·847	2·310
55	0·1027	0·1287	1·856	2·341
60	0·1122	0·1407	1·859	2·345
65	0·1216	0·1524	1·860	2·346
70	0·1312	0·1645	1·863	2·350
75	0·1405	0·1761	1·862	2·349
80	0·1500	0·1881	1·864	2·351
85	0·1590	0·1993	1·859	2·345
90	0·1686	0·2114	1·862	2·349
95	0·1774	0·2224	1·856	2·341
100	0·1862	0·2331	1·848	2·331
105	0·1952	0·2447	1·848	2·331
110	0·2040	0·2558	1·843	2·325
115	0·2129	0·2669	1·840	2·321
120	0·2215	0·2777	1·834	2·314
125	0·2303	0·2887	1·831	2·310
130	0·2390	0·2997	1·827	2·305
135	0·2477	0·3106	1·823	2·300
140	0·2559	0·3209	1·817	2·292
145	0·2641	0·3311	1·811	2·284
150	0·2723	0·3409	1·802	2·273
155	0·2805	0·3517	1·799	2·269
160	0·2889	0·3622	1·795	2·264
165	0·2972	0·3726	1·790	2·258
170	0·3053	0·3828	1·785	2·252
175	0·3134	0·3930	1·779	2·245
180	0·3216	0·4032	1·775	2·240
185	0·3297	0·4134	1·770	2·234
190	0·3377	0·4234	1·765	2·228
195	0·3457	0·4335	1·761	2·223
200	0·3539	0·4431	1·755	2·216
205	0·3616	0·4534	1·751	2·211

39, 933; 40, 792) to employ a copper bicarbonate solution for the estimation of reducing sugars. The disadvantages of such a solution, however, outweigh its advantages, since there is always the possibility of the precipitation of cupric hydroxide, in addition to which calcium and other salts which are present in commercial products are precipitated with the cuprous oxide. More recently Ost has suggested a modification of the Soldaini reagent (Chem. Zeit. 19, 1784, 1829).

Before dismissing copper methods attention may be called to a paper by Kendall (J. Amer. Chem. Soc. 34, 317). Fehling's solution prepared with Rochelle salt is well known to be liable to spontaneous reduction, especially if the copper and Rochelle salt solutions have been kept mixed for some time. Kendall tried various other salts to replace the Rochelle salt, and finally came to the conclusion that a cupric solution containing an alkali carbonate and salicylate remained perfectly stable in absence of extraneous reducing substances. The method adopted is as follows: An appropriate volume of the sugar solution is measured out into a 200 c.c. Erlenmeyer flask and the volume made up to 100 c.c. Five grams of salicylic acid are added, 15 c.c. of copper sulphate solution (containing 2 grms. of crystallised copper sulphate) and 25 c.c. of potassium carbonate solution (containing 15 grms. of the carbonate). This order must be adhered to and the mixture must not be agitated until all the constituents have been introduced, when the flask is rotated, and as soon as all the salicylic acid is dissolved the flask is placed in a boiling water bath for 20 mins. The cuprous oxide is then collected on an asbestos filter, washed and the copper estimated iodometrically by a modification devised by Kendall (*ibid.* 33, 1947).

Knapp's alkaline mercuric cyanide solution (Zeitsch. anal. Chem. 9, 395). This reagent is prepared by dissolving mercuric cyanide (10 grms.) in 100 c.c. of sodium hydroxide solution of sp.gr. 1·145, and making up the solution to one litre. A measured volume of the reagent is heated to boiling and the sugar solution added from a burette until a drop of the filtered solution shows when acidified with acetic acid no coloration with ammonius sulphide. The final point is by no means sharp and the method is but little used at the present time.

Table XXI.—*Invert Sugar.*

Invert sugar mgrms.	Cu weighed grms.	CuO weighed grms.	Cu corresponding to 1 grm. invert sugar	CuO corresponding to 1 grm. invert sugar
50	0·0975	0·1221	1·952	2·442
55	0·1076	0·1349	1·961	2·453
60	0·1176	0·1474	1·964	2·457
65	0·1275	0·1598	1·966	2·459
70	0·1373	0·1721	1·966	2·459
75	0·1468	0·1840	1·962	2·454
80	0·1566	0·1963	1·962	2·454
85	0·1662	0·2084	1·960	2·451
90	0·1755	0·2200	1·955	2·445
95	0·1848	0·2317	1·950	2·439
100	0·1941	0·2430	1·943	2·430
105	0·2034	0·2550	1·942	2·429
110	0·2128	0·2668	1·939	2·425
115	0·2220	0·2783	1·935	2·420
120	0·2311	0·2898	1·931	2·415
125	0·2400	0·3009	1·925	2·407
130	0·2489	0·3121	1·920	2·400
135	0·2578	0·3232	1·915	2·394
140	0·2663	0·3339	1·908	2·385
145	0·2750	0·3448	1·902	2·378
150	0·2832	0·3546	1·891	2·364
155	0·2915	0·3655	1·886	2·358
160	0·3002	0·3764	1·881	2·352
165	0·3086	0·3869	1·875	2·345
170	0·3167	0·3971	1·868	2·336
175	0·3251	0·4076	1·862	2·329
180	0·3331	0·4177	1·855	2·320
185	0·3410	0·4276	1·848	2·311
190	0·3490	0·4376	1·842	2·303
195	0·3570	0·4476	1·836	2·295
200	0·3650	0·4570	1·828	2·285
205	0·3726	0·4672	1·823	2·279

Sachsse's alkaline mercuric iodide solution (Zeits. Ver. Deut. Zuckerind. 26, 872). To prepare this solution, mercuric iodide (18 grms.)—mercuric chloride is precipitated with potassium iodide, the precipitate washed and dried at 100°—is dissolved in a solution containing 80 grms. of potassium hydroxide. The solution is then made up to one litre. A solution of stannous chloride containing an excess of potassium hydroxide is used for determining the final point.

Composition of commercial sugars. It may be pointed out that the values given under 'Polarisation' are those obtained by reading normal (Ventzke) solutions, clarified with the minimum quantity of basic lead acetate solution, in a 2 dm. tube. It will be observed that in the case of beet products the reducing sugars which are calculated as invert sugar are given as a trace. This means that the quantity present was less than 0·05 p.c. In the case of stored beet products, however, it frequently happens that from 0·5 to 5·0 p.c. and even more of reducing sugars are present, their production being due to the action of certain bacteria on the sucrose.

Table XXII.—*Reducing Values of Varying Quantities of Maltose under Standard Conditions.*

Maltose mgrms.	Cu weighed grms.	CuO weighed grms.	Cu corresponding to 1 grm. maltose	CuO corresponding to 1 grm. maltose
70	0·0772	0·0966	1·1029	1·3800
75	0·0826	0·1034	1·1026	1·3796
80	0·0880	0·1102	1·1023	1·3792
85	0·0934	0·1169	1·1020	1·3788
90	0·0988	0·1237	1·1017	1·3784
95	0·1042	0·1305	1·1013	1·3780
100	0·1097	0·1373	1·1010	1·3777
105	0·1151	0·1441	1·1007	1·3773
110	0·1205	0·1509	1·1004	1·3769
115	0·1259	0·1576	1·1001	1·3765
120	0·1313	0·1644	1·0997	1·3761
125	0·1367	0·1712	1·0994	1·3757
130	0·1422	0·1779	1·0991	1·3754
135	0·1476	0·1848	1·0988	1·3750
140	0·1530	0·1916	1·0985	1·3746
145	0·1584	0·1983	1·0981	1·3742
150	0·1634	0·2051	1·0978	1·3738
155	0·1692	0·2119	1·0975	1·3734
160	0·1747	0·2186	1·0972	1·3731
165	0·1801	0·2254	1·0969	1·3727
170	0·1855	0·2323	1·0965	1·3723
175	0·1909	0·2490	1·0962	1·3719
180	0·1963	0·2458	1·0959	1·3715
185	0·2017	0·2526	1·0956	1·3711
190	0·2072	0·2593	1·0953	1·3708
195	0·2126	0·2661	1·0949	1·3704
200	0·2180	0·2729	1·0946	1·3700
205	0·2234	0·2797	1·0943	1·3696
210	0·2288	0·2865	1·0940	1·3692
215	0·2342	0·2933	1·0937	1·3688
220	0·2397	0·3000	1·0933	1·3685
225	0·2451	0·3068	1·0930	1·3681
230	0·2505	0·3136	1·0927	1·3677
235	0·2559	0·3203	1·0924	1·3673
240	0·2613	0·3272	1·0921	1·3669
245	0·2667	0·3340	1·0917	1·3665
250	0·2722	0·3407	1·0914	1·3662
255	0·2776	0·3475	1·0911	1·3658
260	0·2830	0·3543	1·0908	1·3654
265	0·2884	0·3610	1·0905	1·3650
270	0·2938	0·3678	1·0901	1·3646
275	0·2992	0·3747	1·0898	1·3642
280	0·3047	0·3814	1·0895	1·3639
285	0·3101	0·3882	1·0892	1·3635
290	0·3155	0·3950	1·0889	1·3631
295	0·3209	0·4017	1·0885	1·3627
300	0·3264	0·4085	1·0882	1·3623
305	0·3318	0·4154	1·0879	1·3619

Raw beet products. The direct polarisation of beet products as a rule gives a value closely approximating the true percentage of sucrose, an exception to this being when raffinose is present. In products containing raffinose, the direct polarisation must of necessity be in excess of the true percentage of sucrose, since the specific rotatory power of raffinose is greater than that of sucrose.

Table XXIII.—*Bertrand's Table for Estimating Invert Sugar, Glucose, Galactose, Maltose, and Lactose.*

Milligrams of sugar	Milligrams of copper corresponding to				
	Invert sugar	Glucose	Galactose	Maltose	Lactose
10	20·6	20·4	19·3	11·2	14·4
15	30·5	30·2	28·6	16·7	21·4
20	40·4	40·1	37·9	22·2	28·4
25	49·8	49·6	47·0	27·7	35·2
30	59·3	59·1	56·2	33·3	42·1
35	68·5	68·3	65·0	38·7	48·7
40	77·7	77·5	73·9	44·1	55·4
45	86·5	86·4	82·5	49·5	61·9
50	95·4	95·4	91·2	55·0	68·5
55	104·0	104·1	99·7	60·3	74·9
60	112·6	112·8	108·3	65·7	81·4
65	120·9	121·3	116·6	71·1	87·7
70	129·2	129·8	125·0	76·5	94·1
75	137·2	137·9	133·1	81·8	100·4
80	145·3	146·1	141·3	87·2	106·7
85	153·2	154·0	149·4	92·6	112·9
90	161·1	162·0	157·6	98·0	119·1
95	168·8	169·9	165·6	103·2	125·2
100	176·5	177·8	173·6	108·4	131·4

The composition of normal beet products of different grade is as follows:—

Beet crystals. This product contains 99·8–99·9 p.c. of sucrose with 0·05 to 0·07 p.c. of ash. It is obtained in the beet factory, notably when the Steffen process is employed, by steam washing the first masse cuite in a centrifugal machine.

The raw beet sugars which go to the refiner, have the average composition shown below. The so-called 'rendement' or refinery yield is obtained by deducting five times the ash from the polarisation or sucrose percentage. This method of determining the refinery yield was first suggested by Scheibler, and was based on the fact that beet molasses[1] in his time contained on an average 50 p.c. of sucrose and 10 p.c. of ash (see below). He therefore assumed that the mineral matter in raw sugars prevented five times its weight of sugar from crystallising. It is now known that the so-called other organic matters, especially those whch are colloidal, have a far greater melassigenic effect than the mineral matters, *per se.*

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[1] Molasses is the final product in the manufacture of sugar. Although containing sugar, this cannot be separated from it by direct crystallisation.

Raw Beet Products.

	I		II		III	
	First runnings		Second runnings		After products	
Polarisation	96·0	95·5	93·5	91·0	90·0	85·5
Reducing sugars	trace	trace	trace	trace	trace	trace
Ash	0·8	1·2	1·7	2·5	3·0	4·8
Water	1·7	1·7	2·5	3·5	3·5	4·2
Other organic matter	1·5	1·6	2·3	3·0	3·5	5·5
	100·0	100·0	100·0	100·0	100·0	100·0

Molasses.

Polarisation	50·0
Reducing sugars	trace
Ash	10·0
Water	20·0
Other organic matter	20·0
	100·0

Raw products are also met with intermediate in composition between the three grades of solid sugars above referred to. So perfect are the systems now employed in the extraction of sugar from beet that the sucrose content of the molasses is often as low as 46 p.c. It has been mentioned already that beet products are liable to contain raffinose (see this vol. p. 246). Since this sugar is more soluble than sucrose, and as it is present in small amount, it necessarily accumulates in the molasses. Hence those products which are recovered from molasses are more likely to contain raffinose.[1] In some samples of beet molasses, as much as 15 p.c. of raffinose has been found by the optical method. It will have been noticed that in normal beet products the other organic matters are invariably in excess of the ash. When this is not the case, the presence of raffinose is to be suspected. Raw beet sugars containing raffinose—and these are most frequently molasses recovery products or low after products—are, as a rule, fine grained and woolly in appearance.

The following are some analyses of raw beet sugars containing raffinose [1]:—

	I	II
Polarisation	92·1	89·4
Sucrose	91·0	86·8
Raffinose	0·6	1·4
Reducing sugar	trace	trace
Ash	1·7	2·1
Water	3·5	5·0
Other organic matter	3·2	4·7
	100·0	100·0

In certain rare cases, 3 p.c. of raffinose and more has been found in sugars recovered from molasses.

Raw cane products. These are subject to a much greater variation in composition than are raw beet products. A few typical examples only will be given.

	Java basket sugar.		Cuban centrifugal sugar.		Cuban molasses sugar.	
Polarisation	98·0	96·0	97·0	96·50	86·5	80·5
Reducing Sugar	0·5	1·3	1·0	1·30	2·2	4·5
Ash	0·3	0·6	0·5	0·55	2·7	3·5
Water	0·2	1·0	0·5	0·60	4·2	3·0
Other organic matter	0·5	1·1	1·0	1·05	4·4	8·5
	100·0	100·0	100·0	100·00	100·0	100·0

Low, dark coloured solid cane products are met with in commerce under the following descriptions: Madras Jaggery, Java Stoopes, Panela, Penang, Brazilian syrups, Mauritius syrups and Egyptian. The quantity of these low products imported into this country is much less than in former times, since with improved machinery and methods a larger proportion of high grade products is now turned out at the different cane factories all over the world. On this account also such as are imported are much less pure than formerly. The average analytical values obtained with these low products are within the following limits:—

Polarisation	85 to 60 p.c.
Invert sugar	10 to 15 ,,
Soluble ash	3 to 6 ,,

The values given under 'Polarisation' in the case of raw cane sugars are always less than the sucrose percentages determined by the Clerget method, since these products invariably contain reducing sugars which are more or less lævo-rotatory. The polarisations cannot, however, be corrected for these reducing sugars, as their rotatory constants are not always those of invert sugar.

Many raw cane sugars are sold for direct consumption, but the most popular types of these are Demarara sugars and cane products resembling them. These sugars polarise from 95–98 p.c. and contain from 1·5 to 0·5 p.c. of reducing sugar and from 1·5 to 1·0 p.c. of moisture. Occasionally the percentage of re-

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[1] The fact that raffinose is found in the largest quantity in sugars recovered from molasses by one of the alkali earth processes, led chemists to believe that this sugar was formed by the action of the alkali earths; but von Lippmann has shown that raffinose is present in beet juice (Annalen, 232, 169). However, raffinose contains a galactose residue, and bearing in mind Lobry de Bruyn's discovery of the reciprocal conversion of dextrose, lævulose and galactose under the action of alkalis, the possibility is by no means excluded that galactose may be formed by the action of the alkali earths on dextrose and lævulose in the sugar works and that this galactose may condense with sucrose forming raffinose.

[1] The sucrose and raffinose were estimated by the method of double polarisation.

ducing sugars is higher. This is likely to be the case with products which have been stored. Products of like appearance to these types of sugar, which consist however of dyed beet sugar, have for some time been on the market. The dyes employed for the purpose are brilliant yellow S, an azo dye, and phosphine. The former gives a fine violet red colour with acids, whilst the latter remains unchanged on addition of acids. It may be detected, however, by dissolving the suspected sugar in water, rendering the solution alkaline and shaking it with ether, when a yellow coloured ethereal extract, having a greenish fluorescence, is obtained. It should be pointed out that cane products as well as beet are now dyed in the manner described, and in some cases colouring with molasses is resorted to. Another method of imparting an attractive 'bloom' to a raw cane sugar is to treat it with stannous chloride. The writer has found quantities of stannous chloride approximating to 0·001 p.c. in raw sugars.

Cane crystals. These resemble the corresponding beet product, but give a lower polarisation, *e.g.* 99·6 to 99·8 p.c., owing to the presence of a small amount of reducing sugars. They may be distinguished easily from the beet product by their pleasant aroma.

Refined sugars. As produced in this country, refined sugars are sent out at so high a degree of purity that it has been said that no other chemical substance is sold so pure. The ash content is usually less than one part in ten thousand. To give them a white lustre they are often mixed with a minute trace of ultramarine or other blue colouring matter.

Estimation of galactose and galactans. It is a special property of galactose and of all compounds containing a galactose residue to give mucic acid when oxidised with nitric acid. When the oxidation is carried out under standard conditions, the galactose or galactose residue may be estimated from the weight of mucic acid obtained. Among the sugars containing a galactose residue may be mentioned lactose, melibiose, raffinose, rhaminose, &c., whilst a number of polysaccharides, *e.g.* galactans and galactopentosans contain this residue. Many of these are constituents of the gums of commerce, whilst the so-called pectins found in apples, pears, grapes and other fruits, as well as in beetroots, carrots and the tissues of many plants, yield galactose and arabinose on hydrolysis with acids. Just as the formation of furfural constitutes a specific method for the detection and estimation of pentoses and pentosans, so also does the formation of mucic acid form a specific method for the detection and estimation of galactose and galactans. The first chemists to suggest this method of analysis were Tollens and his pupils, and the latest instructions for carrying out the method as revised by the A. O. A. C. (Bull. 107 [revised], U.S. Bur. of Chem., p. 55) are the following:

'Extract a convenient quantity of the substance, representing from 2·5 to 3 grms. of the dry material, on a hardened filter with five successive portions of 10 c.c. of ether; place the extracted residue in a beaker about 5·5 cm. in diameter and 7 cm. deep, together with 60 c.c. of nitric acid of 1·15 sp.gr., and evaporate the solution to exactly one-third its volume in a water bath at a temperature of 94°-96°C. After standing 24 hours, add 10 c.c. of water to the precipitate, and allow it to stand another 24 hours. The mucic acid has in the meantime crystallised, but it is mixed with considerable material only partially oxidised by the nitric acid. Filter the solution, therefore, through filter paper, wash with 30 c.c. of water to remove as much of the nitric acid as possible, and replace the filter and contents in the beaker. Add 30 c.c. of ammonium carbonate solution, consisting of 1 part ammonium carbonate, 19 parts of water and 1 part strong ammonium hydroxide, and heat the mixture on a water bath at 80°C., for 15 mins., with constant stirring. The ammonium carbonate takes up the mucic acid, forming the soluble mucate of ammonia. Then wash the filter paper and contents several times with hot water by decantation, passing the washings through a filter paper, to which finally transfer the material and thoroughly wash. Evaporate the filtrate to dryness over a water bath, avoiding unnecessary heating which causes decomposition, add 5 c.c. of nitric acid of 1·15 sp.gr., thoroughly stir the mixture and allow to stand for 30 mins. The nitric acid decomposes the ammonium mucate, precipitating the mucic acid; collect this on a tared filter or Gooch crucible, wash with from 10 to 15 c.c. of water, then with 60 c.c. of alcohol and a number of times with ether; dry at the temperature of boiling water for 3 hours, and weigh. Multiply mucic acid by 1·33, which gives galactose, and multiply this product by 0·9 which gives galactan.'

As will be seen, the method is empirical, the yield of mucic acid falling short in all cases of the theoretical.

Estimation of pentoses and pentosans. The pentoses, arabinose and xylose, containing as they do a free carbonyl group, may be estimated by cupric reduction methods. Pentosans, on the other hand, do not reduce alkaline copper solutions. Since, however, pentoses as well as pentosans are usually associated with hexoses, a selective method is necessary for their estimation. It has long been known that many carbohydrates yield furfural when heated with acids, and traces are formed from the ordinary hexoses under these conditions. The pentoses and pentosans, however, when distilled with hydrochloric acid under appropriate conditions can be made to yield 75 to 90 p.c. of the theoretical quantity of furfural indicated by the equations:

$$\underset{\text{Pentosan}}{C_5H_8O_4}=\underset{\text{Furfural}}{C_5H_4O_2}+2H_2O$$

$$\underset{\text{Pentose}}{C_5H_{10}O_5}=\underset{\text{Furfural}}{C_5H_4O_2}+3H_2O$$

For the elaboration of methods depending on this principle, we are indebted to Tollens and his pupils. Standard conditions of distillation having been established, it was proposed to precipitate the furfural as phenylhydrazide. This, however, necessitated neutralising the distillate, besides involving the difficulty that furfuralphenylhydrazide is a very unstable substance of low melting-point. Furfural is now precipitated as phloroglucide. The latest modification of the method is that of Tollens and Kröber (J. für Landwirtsch. 1909, 335, 1901, 7). The following are its details. A

Wurtz flask of 300 c.c. capacity is provided with doubly-bored cork so as to take a dropping funnel and the connecting tube to the condenser. The dropping funnel has a cylindrical reservoir with two graduation marks at 30 c.c., and 60 c.c. respectively. The flask is heated in a bath of Rose's alloy which melts near 100°C. Its composition is 1 part lead, 1 part tin and 2 parts bismuth. From 2 to 5 grms. of the substance under investigation, according to the quantity of pentose or pentosan it contains, are placed in the Wurtz flask together with 100 c.c. of hydrochloric acid (sp.gr. 1·06). The flask is connected with the condenser and dropping funnel, which latter is charged with hydrochloric acid (sp.gr. 1·06) up to the upper mark at 60°C. The alloy having been previously heated just above its fusing point, the flask is immersed in it. Distillation is now conducted at such a rate that 30 c.c. pass over in from 10–11 mins. after which a further 30 c.c. of acid is introduced by means of the dropping funnel. The distillate is received in a 100 c.c. graduated cylinder, the contents of which are transferred to a beaker from time to time. The process is continued in this way until a drop of the distillate no longer gives a pink coloration with aniline acetate paper.[1] As a rule, it is necessary to distil over from 1 to 12 portions of 30 c.c., depending on the quantity of pentose or pentosan present in the material.

Purification of phloroglucinol (Bull. 107 [Revised], U.S. Bur. of Chem., p. 54). Phloroglucinol, as purchased, is liable to contain diresorcenol and should be tested for this as follows: A small quantity is dissolved in a little acetic anhydride, heated almost to boiling and a few drops of concentrated sulphuric acid added. A violet coloration indicates the presence of diresorcinol. A sample of phloroglucinol which gives more than a faint coloration must be purified by the following method: hydrochloric acid (300 c.c. sp.gr. 1·06) is heated in a beaker and the phloroglucinol (11 grms.) added in small quantities at a time stirring constantly until almost complete solution has been effected. The hot solution is poured into a sufficient volume of hydrochloric acid of the specific gravity above alluded to that the total volume is 1500 c.c. The liquid is then allowed to remain aside for several days when the diresorcinol will have crystallised out. The solution should be filtered immediately before using. It may become yellow, but this is of no consequence.

Precipitation of the phloroglucide. To the distillate from the sample under investigation contained in a 500 c.c. beaker is added sufficient of the phloroglucinol solution that the quantity of phloroglucinol is about double that of the furfural expected. The solution becomes at first yellow and then changes to a greenish black when the phloroglucide $C_{11}H_3O_4$ begins to deposit. It is then made up to 400 c.c. with hydrochloric acid (sp.gr. 1·06), and allowed to remain aside over night. The supernatant liquid is then tested with aniline acetate paper to ascertain if all the furfural has been precipitated, and if so, it is filtered through a tared Gooch crucible. The phloroglucide having been collected on the asbestos, it is washed with 150 c.c. of water, taking care that the washings never drain entirely from the crucible until the final quantity of water is placed over the precipitate. The crucible is then dried in a boiling water oven for 4 hours, it being placed on a support so that the perforated portion is free to the air. After cooling in a desiccator, the crucible is again weighed. The weight of pentosan or pentose is ascertained from the following table, which is abridged from the original table of Kröber.

TABLE XXIV.—*Kröber's Table for estimating Pentoses and Pentosans.*

Furfural phloroglucide	Furfural	Arabinose	Araban	Xylose	Xylan
0·030	0·0182	0·0391	0·0344	0·0324	0·0285
0·040	0·0235	0·0501	0·0441	0·0416	0·0366
0·050	0·0286	0·0611	0·0538	0·0507	0·0446
0·060	0·0338	0·0721	0·0634	0·0598	0·0526
0·070	0·0390	0·0831	0·0731	0·0690	0·0607
0·080	0·0442	0·0941	0·0828	0·0781	0 0687
0·090	0·0494	0·1051	0·0925	0·0872	0·0767
0·100	0·0546	0·1161	0·1022	0·0964	0·0848
0·110	0·0598	0·1270	0·1118	0·1055	0·0928
0·120	0·0650	0·1380	0·1214	0·1146	0·1008
0·130	0·0702	0·1490	0·1311	0·1237	0·1089
0·140	0·0754	0·1600	0·1408	0·1328	0·1169
0·150	0·0805	0·1710	0·1505	0·1419	0·1249
0·160	0·0857	0·1820	0·1602	0·1510	0·1329
0·170	0·0909	0·1930	0·1698	0·1601	0·1409
0·180	0·0961	0·0239	0·1794	0·1692	0·1489
0·190	0·1013	0·2147	0·1889	0·1783	0·1569
0·200	0·1065	0·2255	0·1984	0·1874	0·1649
0·210	0·1116	0·2363	0·2079	0·1965	0·1729
0·220	0·1168	0·2471	0·2174	0·2057	0·1810
0·230	0·1220	0·2579	0·2270	0·2148	0·1890
0·240	0·1271	0·2687	0·2365	0·2239	0·1970
0·250	0·1323	0·2795	0·2460	0·2330	0·2050
0·260	0·1374	0·2903	0·2555	0·2420	0·2130
0·270	0·1426	0·3011	0·2650	0·2511	0·2210
0·280	0·1478	0·3119	0·2745	0·2602	0·2290
0·290	0·1529	0·3227	0·2840	0·2693	0·2370
0·300	0·1581	0·3335	0·2935	0·2784	0·2450

When a mixture of pentosans or pentoses is being dealt with, the mean of ariban and xylan values and the arabinose and xylose values respectively should be reported. For weights of phloroglucide outside the limits of the table, Kröber gives the following formulæ.

For a weight of phloroglucide *a* under 0·03 grm.

Weight of furfural $=(a\ 0{\cdot}0052\times0{\cdot}5170)$
„ pentoses $=(a\ 0{\cdot}0052\times1{\cdot}0170)$
„ pentosans $=(a\ 0{\cdot}0052\times0{\cdot}8948)$

For a weight of phloroglucide *a* over 0·3 grm.

Weight of furfural $=(a\ 0{\cdot}0052\times0{\cdot}518)$
„ pentoses $=(a\ 0{\cdot}0052\times0{\cdot}10026)$
„ pentosans $=(a\ 0{\cdot}0052\times0{\cdot}8824)$

The factor 0·0052 is the weight of phloroglucide which remains dissolved in the 400 c.c. of acid solution.

Jolles, in 1905 (Sitzungsber Wien Akad. 114, II*b*, 1191), worked out a method of estimating furfural which consisted in adding a known quantity in excess of sodium hydrogen sulphite to the faintly acid distillate obtained as already described. The excess (uncombined) sulphite is then estimated by titration with N/10 iodine solution. The method as at present worked out appears to present no advantages over the phloroglucide method.

In 1910, Flohil (Chem. Weekblad. 7, 1057) proposed to estimate furfural by measuring its

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[1] To prepare aniline acetate paper equal volumes of aniline and water are mixed in a test tube and glacial acetic acid added drop by drop until the milky emulsion becomes a clear solution. Strips of filter paper are then moistened with this solution and allowed to dry.

reducing action on Fehling's solution under standard conditions. His results were revised by Eynon and Lane (Analyst, 37, 41), but even as these chemists left it, the method is inferior in accuracy to the phloroglucide method.

For the estimation of methyl pentoses or methyl pentosans, see Tollens and Ellet (Ber. 38, 492); Tollens and Mayer (*ibid.* 40, 2441); Jolles (Annalen, 351, 41).

Analysis of mixtures of sugars. I. Invert sugar. Commercial invert sugar is one of the most valuable and widely-used brewing sugars. It is prepared by hydrolysing raw cane sugars by an acid (usually sulphuric but occasionally hydrochloric)—raw beet sugars cannot be used for this purpose—neutralising with calcium carbonate filtering, and after passing through a column of animal charcoal concentrating the filtrate to such a degree that a 10 p.c. solution of the final product shows an extract of 70–72 Brewers' lb. per 2 cwt. The extract is determined by weighing out 10 grms. of the sample, dissolving in water, diluting to 100 c.c. and determining the specific gravity of the solution. The excess specific gravity over that of water (taken as 1000), multiplied by the factor 2·24, gives the extract of the sample in lb. per 2 cwt. This method is quite an arbitrary one, and if a solution of any other concentration than 10 p.c. is made use of, the factor directly proportional to 2·24 does not give the same result.

The estimation of the ash and water is conducted as described on p. 262 (see more especially under syrupy products). The sugars are estimated by a scheme devised by Morris (J. Inst. Brewing, 4, 162). Morris employed the gravimetric method of Brown, Morris and Millar (see p. 253), whilst the writer has always employed the volumetric method (see p. 247). The details of the scheme when the latter method is employed are as follows:—

Total reducing sugars. A convenient volume (usually 10 c.c.) of a 10 p.c. solution of the sample is made up to 1000 c.c. and titrated with 10 c.c. of Fehling's solution in the manner described on p. 248. Let the percentage of apparent invert sugar calculated on the sample be denoted by the symbol I.

Sucrose. The same volume of a 10 p.c. solution as that employed for the estimation of the total reducing sugars is diluted with 100 c.c. of water and 20 c.c. of N/2 hydrochloric acid. The mixture is raised to a boiling temperature and maintained in ebullition for one minute, after which it is cooled, neutralised by the addition of 20 c.c. of N/2 sodium hydroxide, and made up to 1000 c.c. The solution is then titrated against 10 c.c. of Fehling's solution. The percentage of apparent invert sugar calculated on the sample may then be denoted by the symbol I′. The percentage of sucrose is then calculated by the following formula: $S=\frac{95(I'-I)}{100}$. Commercial invert sugar contains unfermentable reducing substances, and it is therefore necessary to correct the results for these. The fermentation test is best carried out as follows: 25 grms. of the sample are dissolved in about 200 c.c. of water in an Erlenmeyer flask and the solution is sterilised by boiling. About 5 c.c. of yeast decoction (1–5) is now added, and about 3 grms. of washed pressed yeast. The flask is closed with a cotton wool plug and placed in a thermostat at 70°F. for 3–4 days, after which it is transferred to a 250 c.c. flask, a little alumina cream added and made up to 250 c.c. The reducing power of the filtrate is then determined and calculated on the sample. The value so obtained may be denoted as F. Then $I-F=K$, the reducing power due to dextrose and lævulose in the sample. The number of c.c.'s of Fehling's solution corresponding with 1 grm. of the sample is now calculated and denoted as G.

The rotation of a 10 p.c. solution of the sample in divisions Ventzke (2 dm. tube) is determined before and after fermentation. The direct rotation value corrected for that of the fermented solution and for that of the percentage of sucrose found (see above) is denoted by the symbol R.

From these data the percentages of dextrose and lævulose in the sample may be calculated by the following simultaneous equations:—

$$(a)\ 1{\cdot}966D+1{\cdot}838L=G.$$
$$(b)\ 0{\cdot}305D+(-0{\cdot}532L)=R.$$

The coefficients of D and L in equation are the gram Fehling equivalent of dextrose and lævulose respectively at a certain concentration. These coefficients may be obtained from the table of Ling and Jones (p. 248). If the gravimetric method is used, the constants worked out by Morris (J. Inst. Brewing, 4, 162) for the Brown, Morris and Millar method are applied.

Invert sugar is supplied to the brewer in three grades, and the following are typical analyses of each.

	No. 1	No. 2	No. 3
Dextrose	36·85	36·96	35·44
Lævulose	36·22	35·01	34·85
Sucrose	3·39	1·89	4·54
Albuminoids . . .	0·20	0·26	0·27
Ash	1·57	2·20	2·51
Other organic matter[1] .	4·25	5·23	3·60
Water	17·52	18·45	18·79
	100·00	100·00	100·00

	No. 1	No. 2	No. 3
[1] Containing unfermentable reducing carbohydrates expressed as invert sugar .	3·36	3·62	3·40 p.c.
Brewers' extract per 2 cwt.	72·8	72·6	72·6 lb.
Tint (Lovibond, 10 p.c. solution 1″ cell) . . .	3·5	8·5	13·0 N.
Specific rotary power $[\alpha]_D$	−11·6°	−11·4°	−10·4°.
Ferric Oxide (Fe_2O_3) .	0·002	0·003	0·003 p.c.

These results were obtained with samples of the three grades of invert sugar of exceptionally high quality. It sometimes happens that there is a shortage of raw cane sugar of low ash content on the market, and some considerable latitude has to be allowed with regard to the permissible limits of ash in the three grades of sugar. The percentages of ash should, however, never exceed the following limits, which will seldom be reached.

No. I, 2·00 p.c.; No. II, 2·75 p.c.; No. III, 3·50 p.c. The percentage of albuminoids should not exceed the following: No. I, 0·30 p.c.; No. II, 0·50 p.c.; No. III, 0·75 p.c. (compare below).

A widespread belief exists among brewers that invert sugar prepared from beet products gives rise to troubles when employed for brewing, and the writer from practical experience can confirm this in so far as invert sugars prepared from 'raw' beet products are concerned. On the other hand, no exception can be taken to invert sugars prepared from beet crystals and other high grade sugars derived from beet, except that they do not add to the palate fullness or lusciousness of the finished beers. In seeking an explanation of these facts, it has to be remembered that the substances other than the sugars present in 'raw' products derived from the sugar cane are helpful in producing that fullness of palate which—especially in the case of mild ales and stouts—is now demanded by the public. It is otherwise in the case of 'raw' beet products. Here the substances, other than the sugars, have a nauseous flavour which tends to impair the palate of beers. These substances appear also to cause certain secondary troubles in the finished beers.

When low grade beet sugars have been used for the manufacture of invert sugar, the product will possess a characteristic odour and flavour. If, however, higher grade (first runnings) raw beet sugars have been employed, it is difficult to arrive at a decision from the odour and flavour alone, more especially if the sample has been made from a mixture of first running beet sugars and raw cane sugars. The writer would point out in this connection that the percentage of albuminoids (*i.e.* nitrogen × 6·25) in beet products greatly exceeds that in cane products Thus he has found the following percentages in low grade cane products: Mauritius, 0·48 p.c.; Penang, 0·39 p.c.; Brazil, 0·63 p.c.; Panela, 0·61 p.c.; Jaggery, 0·59 p.c.; cane molasses, 4–5 p.c. On the other hand, he has found the following percentages in beet products: first runnings, 0·89 to 1·00 p.c.; second runnings, 1·77 to 2·00 p.c.; beet molasses, 6·23 to 9·50 p.c.[1]

II. *Honey*. Since the principal constituent of honey is invert sugar, the scheme just described for the analysis of commercial invert sugar may be used for its analysis. The following analyses of honey from various sources are reported by Campbell Brown (Analyst, 3, 267).

TABLE XXV.—*The Composition of Honey.—Percentages.*

Source	Water	Lævulose	Dextrose	Sucrose	Wax, pollen, and other insoluble matters	Ash	Other organic matter
England . . .	19·10	36·60	36·55	—	trace	0·15	7·60
Wales . . .	16·40	37·20	39·70	—	trace	0·14	6·56
Normandy . .	15·50	36·88	42·50	—	trace	0·17	4·95
Germany . . .	19·11	33·14	36·58	—	trace	0·17	11·00
Greece . . .	19·80	40·00	32·20	—	1·05	0·15	7·80
Portugal . . .	18·80	37·26	34·94	1·20	1·00	0·14	6·66
Jamaica . . .	19·46	33·19	35·21	2·20	2·10	0·26	7·58
California . . .	17·90	37·85	36·01	—	trace	0·11	8·13
Mexico . . .	18·47	35·96	35·47	—	trace	0·07	10·03

Tibbles (Foods, their Origin, Composition and Manufacture, p. 729) gives the following analyses of authentic honeys:—

Seiber (Biedermann's Centralblatt 1885, 134) average of sixty analyses.

Dextrose	Lævulose	Sucrose	Water
34·71	39·24	1·08	19·28 per cent.

Hoitsema (Zeitsch. anal. Chem. 38, 429).

	Invert sugar	Sucrose	Wax, pollen,&c.	Ash	Water
Minimum	71·20	0·20	0·02	0·13	8·30 p.c.
Maximum	74·50	2·60	0·46	0·34	17·80 p.c.

Canadian Inland Revenue Bulletin, 47.

	Invert sugar	Sucrose	Ash	Water
Minimum	66·37	0·50	0·03	12·00 p.c.
Maximum	78·80	7·64	0·05	33·00 p.c.

Narbonne Honey (The Practical Grocer, ii. 161).

Invert sugar	Sucrose	Wax, pollen, &c.	Ash	Water
74·00	7·10	1·50	0·30	17·10 p.c.

The presence of sucrose in honey seems remarkable. The writer has found as much as 10 per cent. of sucrose in some samples of British honey. Such a high percentage is, however, exceptional.

Honeys in the United States have been found to contain dextrinous carbohydrates which are precipitable by alcohol from their aqueous solutions and are unfermentable by brewers' yeast. The specific rotatory power of honey dextrin, according to Browne, is $[\alpha]_D$ 115°–160°. Browne (Bull. 110, U.S. Bur. of Chem.) gives a number of analyses of dextrinous honeys of different kinds, and he shows that the quantity of dextrin varies from 0·34 to 12·95 p.c.

Honey is frequently adulterated with artificial invert sugar, and for the detection of the latter certain colorimetric tests have been devised. Furfural is said to be a constituent of artificial invert sugar and C. A. Browne (Bull. 110, U.S. Bur. of Chem.) suggests testing for this with aniline acetate. The reagent must be freshly prepared by the following method: 5 c.c. of aniline are shaken with 5 c.c. of water and 2 c.c. of gluceal acetic acid added. This amount of acid is just sufficient to produce a bright solution. One to two c.c. of the reagent are allowed to flow down the walls of a test tube into a solution of the honey in an equal weight of water. If, after shaking, a red ring forms below the aniline layer and gradually spreads to the whole solution, invert sugar is present.

Fiehe (Chem. Zeit. 32, 1045; Zeitsch. Nahr. Genussm. 1908, 75) points out that during the manufacture of invert sugar some of the lævulose is converted into β-hydroxy-δ-methylfurfural, which gives a red coloration with a solution of one part of resorcinol in 100 parts of hydrochloric acid (sp.gr. 1·19). This has been confirmed as a test for artificial invert sugar (see Witte, Zeitsch. Nahr. Genussm. 1909, 625; Reinhardt, *ibid.* 1910, 113; Muttelet, Ann. Falsif. 3, 206).

More recently, Litterscheid (Chem. Zeit. 37. 321) has stated that the following colorimetric method may be used for the detection of artificial invert sugar in honey: 10–20 grms. of the honey are successively triturated with two portions of 10 c.c. of ether in which one or two crystals of β-naphthol have been previously dissolved. The unfiltered extract is transferred to a shallow porcelain dish and left in a dark place until the ether has evaporated. Four or

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[1] The molasses values are quoted from Stammer's analyses.

five c.c. of concentrated 88–90 p.c. sulphuric acid are added to the residue, the latter being completely moistened with the acid, and allowed to stand. A dirty yellowish or reddish-yellow colour, which in half an hour becomes dirty yellowish-green, is obtained with natural honey, whilst a Bordeaux red to bluish-violet colour appears in the course of half an hour in the case of honey containing commercial invert sugar. A positive result was obtained with mixtures of natural honey and 5 p.c. of commercial invert sugar, and sometimes also when the result obtained by Fiehe's method (*l.c.*) was inconclusive.

These tests are for the detection of artificial honey. For the detection of genuine honey, it has been suggested to apply a physiological (serum) test (Langer, Arch. Hygiene, 71, 308), and it has also been proposed to characterise natural honey by determining its catalytic and invertive powers (Auzinger, Zeitsch. Nahr. Genussm. 1911, 65).

Useful bibliographies of honey are published by the U.S. Department of Agriculture. Bull. 13 gives a list of papers from 1867 to 1892. Bull. 110 continues the bibliography to 1908, whilst it was brought to 1910 by Muttelet (Monit. Scient. 74, 152). The lists are published in the Journal of the Society of Chemical Industry (1892, 11, 761; 1911, 30, 702).

III. *Brewing glucose or glucose chips.* This description of sugar occupies a position next in importance to invert sugar as a brewing sugar. It is prepared by the hydrolysis of different kinds of starch with acids. This material consists for the most part of dextrose, but contains also maltose and dextrins or more probably malto-dextrins. The occurrence of maltose as an intermediate product in the hydrolysis of starch by acids was assumed by numerous observers on the sole evidence of the optical and reducing values obtained with them. Ost, however (Zeitsch. angew. Chem. 1904, 1663), succeeded in isolating maltose from the products of the hydrolysis of starch by acids. Chemists are therefore quite justified in interpreting these products from their constants in terms of dextrose, maltose and dextrins.

The analysis of these products is conducted on the same lines as that of invert sugar, but since the assumed proximate constituents are different, the results must be calculated by different equations. In the following equations D is the symbol for dextrose and M that for maltose. The same remarks apply in regard to the coefficient of D as in the case of the corresponding equation for invert sugar. The coefficient of M (which is the symbol for maltose) is a constant for the whole range of dilutions employed (see table of Ling and Jones, p. 248).

Inasmuch as these products contain dextrinous carbohydrates, the residue after fermentation is always dextro-rotatory, and in some cases a considerable correction has to be applied to the rotatory power to obtain the value denoted by the symbol G. Brewing glucoses, unlike invert sugars, however, do not contain sucrose.

The equations for calculating the percentage of dextrose and maltose in these products are as follows :—

$$(a)\ 1{\cdot}966\,D+1{\cdot}225\,M=G$$

$$(b)\ 0{\cdot}305\,D+0{\cdot}797\,M=R$$

The following is an analysis of a high grade sample of glucose chips :

Dextrose	66·76
Maltose	3·96
Albuminoids	0·53
Ash	1·75
Dextrinous carbohydrates and other organic matter	13·60
Water	13·40
	100·00
Brewers' extract per 2 cwt.	76·1 lb.
Tint (Lovibond, 10 p.c. solution 1′ cell)	10·0 N.
Specific rotatory power	$[\alpha]_D$ 50·8°

This analysis can scarcely be taken as typical, since these products vary enormously in composition. Thus, the percentage of total sugars ranges from 65 to 75 and the extract from 72 to 76 lbs. The percentage of maltose may also vary from 12 p.c. to *nil*. The specific rotatory power ranges from $[\alpha]_D$ 44° to 56°.

IV. *Glucose syrup or dextrin-maltose.* This product, which is semi-hydrolysed starch, is largely employed in confectionery and also, though to a lesser extent, in brewing. The analysis is conducted on the same lines as that of solid glucose. The percentage of dextrin is calculated from the rotatory power of a 10 p.c. solution after fermentation by dividing by the factor 11·66 (see p. 237). The factor to be employed really diminishes with the reducing power of the dextrin, but for practical purposes this may be ignored. A typical analysis of glucose syrup, the composition of which is remarkably constant, is the following :

Dextrose	23·10
Maltose	26·03
Dextrin	32·17
Albuminoids	0·22
Ash	0·48
Water	18·00
	100·00
Brewers' extract per 2 cwt.	70·7 lb.
Specific rotatory power	$[\alpha]_D$ 113·1°

Estimation of sugars as phenylosazones. Maquenne (Compt. rend. 112, 799) determined the yield of phenylosazones from dextrose, lævulose and sucrose,[1] and subsequently Lintner and Kröber (Zeit. ges. Brauw. 18, 153) made an attempt to estimate certain sugars as phenylosazones. The method would be chiefly of service in separating dextrose and lævulose which form phenylglucosazone sparingly soluble in hot water from maltose which yields a phenylosazone readily soluble in hot water. In their studies on the hydrolysis of starch by malt diastase, Ling and Davis (J. Inst. Brewing, 8, 475; Chem. Soc. Trans. 85, 16) used the osazone method to demonstrate the production of dextrose at the later stages of the reaction. They also used the osazone method for the approximate estimation of dextrose as phenylglucosazone in presence of the other starch conversion products (*cf.* also Ling, J. Inst. Brewing, 9, 448). The method is useful as a qualitative one for identifying dextrose in presence of maltose, but

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[1] Sucrose gives a certain amount of phenylglucosazone when heated with phenyhydrazine and acetic acid in virtue of undergoing partial hydrolysis.

it can also be made approximately quantitative. For this purpose it is necessary to employ only the purest freshly distilled phenylhydrazine and also to establish the yield of glucosazone in presence of mixtures of the same sugars contained in the substance being investigated. Ling and Rendle (Analyst, 29, 243) were able to prove the presence and approximate percentage of dextrose in commercial malt extracts known to be unadulterated. Baker and Dick (*ibid.* 30, 79), repeating Grimbert's work on the detection and estimation of small quantities of maltose in presence of dextrose, by treating the mixed phenylosazones with dilute (20 p.c.) acetone, found that the method could not be relied upon for quantitative purposes.

Biochemical methods of estimating sugars. The only methods of this class which will be alluded to here are those depending on the selective fermentability of different sugars by different yeasts. The fermentation method has already been mentioned in connection with the estimation of dextrinous carbohydrates in presence of fermentable sugars (see pp. 259–261). The better known monohexoses, *d*-mannose, lævulose, dextrose and galactose, are fermentable by *Saccharomyces cerevisiæ*, *S. pastorianus* and *S. ellipsoideus* (not, however, the monopentoses, arabinose and xylose), as are also the bioses, sucrose and maltose. These latter, however, must in the first place be hydrolysed to dextrose and lævulose and dextrose respectively. Consequently, for a yeast to be able to ferment sucrose, it must contain invertase or sucrase, whilst to ferment maltose it must contain maltase. Lactose is unfermentable by the above-mentioned yeasts which do not contain lactase, but Fischer and Tierfelder (Ber. 27, 2031) describe a yeast which ferments milk sugar as well as the ordinary monohexoses, but does not ferment maltose.

S. Marxianus does not contain a maltase or a lactase. Consequently, whilst it ferments the ordinary monohexoses, the bihexoses, lactose and maltose are unfermentable by it. Baker and Dick (Analyst, 30, 79) found that maltose could be estimated in mixtures of that sugar and the ordinary monohexoses by fermenting the latter by *S. Marxianus.* Dextrins, if present, were found to vitiate the results. In this case, however, the writer would point out that the dextrin must be estimated in a separate experiment in which the maltose as well as the monohexoses is fermented by *S. cerevisiæ.*

Several observers have made use of the fact that lactose is unfermentable by ordinary yeasts, *e.g. S. cerevisiæ*, to estimate that sugar in admixture with the fermentable sugars. The writer finds this method to give fairly satisfactory results. It has been investigated by Baker and Hulton (Analyst, 35, 512).

In all these laboratory fermentations, it is necessary to add a certain quantity of yeast food, which may consist of Hayduck's solution: potassium phosphate (25 grms.), magnesium sulphate (8 grms.), and asparagine (20 grms.) dissolved in water and made up to one litre. One cubic centimetre of this solution to each 25 c.c. of liquid to be fermented is used. The writer usually employs, however, yeast decoction as a yeast food in these cases (see p. 259). The fermentations may be conveniently carried out in Erlenmeyer flasks plugged with cotton wool. The flasks must be of sufficient size that the liquid never reaches the cotton wool during the fermentation.

Estimation of mineral matter (*ash*) *in sugar products.* The estimation of the ash in sugars, molasses, &c., by direct incineration, is not only a lengthy and tedious operation, but it is very difficult and often impossible to obtain concordant results in repetition experiments. Thus the mineral residues obtained by burning commercial sugars consist largely of alkali carbonates, which are fusible and volatile at the temperature at which the incineration is sometimes conducted. When fusion occurs before all the carbon has been burnt, the latter is occluded in a fused mass of mineral matter and complete combustion is then impossible. The procedure recommended by the A. O. A. C. (Bull. 107 [revised] U.S. Bur. of Chem. 67–68) is as follows: 'Heat from 5 to 10 grms. of sugar molasses, &c., in a platinum dish of 50–100 c.c. capacity at 100°C. until the water has been expelled and then slowly over a flame until intumescence ceases. Then place the dish in a muffle and heat at low redness until a white ash is left.'

The method most frequently employed is that first proposed by Scheibler in which the sugar is burnt in the presence of sulphuric acid. When this method is employed it is not necessary to use platinum capsules, but these may be replaced by porcelain or silica capsules. Indeed, in one respect, the latter are superior to platinum for the purpose, for since porcelain and silica do not conduct heat as well as does platinum, there is not so much danger of the ash fusing should the temperature of the muffle suddenly rise. And here it may be pointed out that on no account should sugar be incinerated over a flame, but always in a muffle furnace which should be kept at a low red heat.

The plan of carrying out the estimation of sulphated ash, which the writer has adopted for many years, is as follows. A portion of the sample (5 or 3 grms.) is accurately weighed out in a recently ignited capsule, 2 c.c. of concentrated sulphuric acid, free from fixed mineral matter, are dropped over the surface and subsequently a little distilled water is added. The addition of water is to equalise the reaction; it is not necessary with syrups and molasses or with very moist solid sugars. The capsule is then heated over a flame until intumescence is complete, when it is transferred to a muffle and incinerated at a low red heat. The resulting ash should be feathery. When fusion occurs this is generally attended by low results unless carbon is present. Some chemists after determining the weight of the ash, dissolve it in water and test it with litmus paper for acidity, but if the above instructions are followed, there is no danger of the presence of sulphuric acid when combustion is complete. Obviously the sulphated ash weighs more than that obtained by direct incineration, and to correct for this, Scheibler's suggestion to deduct one-tenth from the weight of the sulphated ash is practically universally adopted. It is convenient to work on 3 grm. portions of sugars, for in this case multiplication of the weight of the resulting ash by 30 gives the percentage of ash on the sample with Scheibler's correction. In the case of some products, *e.g.* brewing sugars, the deduction of one-tenth from the weight of sulphated ash is undoubtedly too large a correction, but the method gives comparative rather than absolute accuracy, and the latter, as already observed, cannot be attained by the direct incineration method.

Sand. When sand is present and it is desired to estimate it, the ash is dissolved in the capsule in a little warm dilute hydrochloric acid, and, after allowing the sand to subside, the supernatant liquor is decanted off. The sand is now washed by decantation, dried, ignited and weighed. Any silica which existed in a soluble state in the sugar passes away mechanically with the washing water. In most books, instructions are given to collect the sand on a paper filter, and after washing out the soluble matter to burn the filter. Filtration is, however, quite unnecessary.

Soluble ash. This is the difference between the total ash and the sand. In case any silica, derived from soluble silicates in the sample, had been included in the latter, a slight error would be introduced. This, however, is quite negligible. On the other hand, low grade raw cane products frequently contain wood, fragments of sugar cane, and other insoluble extraneous matters, and the total ash taken as above includes the ash of these extraneous matters. The true soluble ash must be estimated on a known volume of a standard filtered solution of the sugar. Thus, 25 grms. of the sugar are dissolved in water, made up to 100 c.c., and an aliquot portion of the filtrate corresponding with 5 or 3 grms. evaporated and incinerated with sulphuric acid as already described.

Estimation of ash from the electrical conductivity of commercial sugar solutions. This method was first placed on a practical basis by Main (Seventh Inter. Cong. Appl. Chem. Section V., p. 66; Inter. Sugar J., 11, 334). The subject was investigated by Reichert (Zeitsch. anal. Chem. 28) more than twenty years ago. Main's observations are briefly as follows. For practical purposes, it may be accepted that sugar in solution is a non-electrolyte, and that the conductivity of impure sugar solutions is to be ascribed to the inorganic and organic salts present. If in a series of samples, solutions of the same concentration are made, the resistances of these solutions are inversely proportional to the amount of salts present. The resistances are measured by Kohlrausch's telephone method. Although the sugar in the solutions may be regarded as non-conducting, variations in the quantity of sugar present affect the conductivity of the salts present. The disturbing influence of differences in the quantity of sugar present can be removed by working with solutions of about the same specific gravity. Taking a series of sugars of about the same grade containing from 2 to 5 p.c. of ash, 5 grms. of each are dissolved in distilled water, made up to 100 c.c. and the resistance of the solutions determined at 20°C. Then it is found that the resistances expressed in ohms multiplied by the percentage of ash as determined gravimetrically in the usual manner give approximately a constant which serves for the determination of ash in other samples of similar sugars when the resistance of their solutions is determined in the same manner in the same cell. Thus $A = K/O$, where A is the percentage of ash in the sample, K the constant above referred to, and O the resistance of the solution expressed in ohms. When working with molasses, the samples are diluted to 33 Beaumé and 2 grms. weighed out, diluted to 100 c.c., and the constant determined as in the case of sugars.

The accuracy of which the method is capable may be judged from the following instances cited by Main. Column 1 in the tables gives the resistance in ohms=O. Column 2 gives the percentage of ash estimated gravimetrically=A. Column 3 gives the product $O \times A = K$. Column 4 gives the ash calculated from the mean value of K as already explained.

Sugars.

O	A	K[1]	A′
132	5·17	682	5·15
167	4·07	680	4·07
199	3·43	683	3·42
212	3·19	676	3·21
220	3·07	675	3·09
293	2·33	683	2·32

Molasses.

O	A	K[2]	A′
190	8·76	1664	8·80
191	8·75	1671	8·75
194	8·63	1674	8·62
195	8·62	1681	8·57
196	9·56	1678	8·53
203	8·19	1663	8·24

Lange (Zeits. Ver. Deut. Zuckerind. 1910, 359) finds that reliable results can be obtained by Main's method with products, the ash percentages of which do not differ by more than 0·5 p.c. In order to make the method of greater general applicability, the influence of sugar as a non-conductor on the conductivity of a salt solution was further investigated. Where C is the conductivity of the solution containing p grams in 100 c.c. of the non-conductor, c is the conductivity of the aqueous solution of the salt, and a an empirical coefficient, the relationship may be expressed by Arrhenius' formula $C=c(1-\frac{a}{2}p)^2$. The value of the coefficient a for the group of salts occurring in sugar products was found by Lange to be 0·0314. In the case of products containing more than 3 p.c. of ash, the conductivity of a series of solutions of different ash content has been determined, and the conductivity which the solutions would have if no sugar were present is calculated by the above formula. From the values thus obtained, a table has been constructed. When dealing with any product, it is simply necessary to determine the conductivity of its aqueous solution, and calculate from this and the known sugar content the conductivity of solution without sugar. The percentage of ash may then be ascertained by the aid of these data from a table. Lange has also constructed an empirical table for products containing less than 3 p.c. of ash, with which the influence of the sugar on the conductivity may be ignored. He has also calculated a table for correcting for the influence of temperature between 15° and 25°C. He gives a number of examples

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[1] The mean value for K is 680.

[2] The mean value for K is 1672.

with various products illustrating the accuracy of the method.

Estimation of water and solid matter in saccharine products. The usual method of estimating water in solid commercial products is to heat from 3 to 5 grms. weighed out to the nearest half milligram in a drying oven at 100°C. for 3 to 5 hours, taking the loss in weight as due to water. In the case of small-grained, very moist sugars containing much molasses, this method gives low results. Better results are obtained if the drying be conducted at 105°–110°C.[1] This, however, applies more especially to beet products; in the case of cane products, which usually contain a large amount of reducing sugars, the use of such a temperature would be attended by error due to the decomposition of the latter. If the products be heated in a current of air or other gas, the moisture may usually be expelled from all solid sugar products at 100°C. A simple and convenient apparatus for this purpose has been devised by Siau (J. Soc. Chem. Ind. 30, 61). The official method of A. O. A. C. is to be found in Bull. 107 (revised), U.S. Bur. of Chem., p. 64.

The sugar is conveniently weighed out and dried in a shallow metal dish—a copper dish serves the purpose very well—or the drying may be conducted in a porcelain or quartz dish.

Estimation of water in syrups, molasses, and massecuites. The following directions are given for this purpose by the A. O. A. C. (Bull. 107, *l.c.*). The methods are not suitable, however, for those products which contain large percentages of reducing sugars, *e.g.* cane products.

Drying on pumice stone. 'Prepare pumice stone in two grades of fineness. One of these should pass through a 1 mm. sieve, whilst the other should be composed of particles too large for a millimeter sieve, but sufficiently small to pass through a sieve having meshes 6 mm. in diameter. Make the determination in flat metallic dishes or in shallow, flat-bottomed weighing bottles. Place a layer of the fine pumice stone, 3 mm. in thickness, over the bottom of the dish and upon this place a layer of the coarse pumice stone from 6 to 10 mm. in thickness. Dry the dish thus prepared and weigh. Dilute the sample with a weighed portion of water in such a manner that the diluted material shall contain from 20 to 30 p.c. of dry matter. Weigh into the dish, prepared as described above, such a quantity of the diluted sample as will yield, approximately, 1 grm. of dry matter. Use a weighing bottle provided with a cork through which a pipette passes if this weighing cannot be made with extreme rapidity. Place the dish in a water oven and dry to constant weight at the temperature of boiling water, making trial weighings at intervals of 2 hours. In case of materials containing much lævulose or other readily decomposable substances, conduct the drying *in vacuô* at about 70°C.'

Drying on quartz sand. 'In a flat-bottom dish place 6 to 7 grms. of pure quartz sand and a short stirring rod. Dry thoroughly, cool in a desiccator, and weigh. Then add 3 or 4 grms. of the molasses, mix with the sand, and dry at the temperature of boiling water for from 8 to 10 hours. Stir at intervals of an hour, then cool in a desiccator, and weigh. Stir, heat again in the water oven for an hour, cool, and weigh. Repeat heating and weighing until loss of water in one hour is not greater than 3 mgs.

'Before using, digest the pure quartz sand with strong hydrochloric acid, wash, dry, ignite and keep in a stoppered bottle.'

For the estimation of water in cane products, honey, &c., which contain a considerable amount of reducing sugars, methods of drying in a vacuum have to be resorted to for the reason above alluded to. The method of Carr and Sanborn (Bull. 47, U.S. Bur. of Chem., p. 134) is one of which the reliability has been proved. The method (*l.c.*) is as follows: Clean fine-grained pumice is divided into fragments of the size of No. 4 shot. The finer particles (dust) are separated from the coarser by passing through a 40-mesh sieve; the two grades are heated separately. They are digested with hot 2 p.c. sulphuric acid and washed until the washings are neutral. The washing may be carried out rapidly by decantation. The washed pumice is dried by heating to redness in a Hessian crucible, after which it is placed while hot in a desiccator. A thin layer of the dust is placed over the internal surface of the dish in which the estimation is to be conducted. Above this layer are placed sufficient of the larger particles that the dish is almost filled. The dish thus charged with pumice is ignited and weighed, after cooling in a desiccator. The substance to be dried is diluted (if necessary) to a specific gravity of about 1·08 by the addition of water or of alcohol, if no precipitation is caused by the latter. Two to three grms. are distributed uniformly by means of a pipette weighing bottle over the pumice in the dish, the area of which is about 3 sq. ins., *i.e.* 1 grm. for each square inch of area. The amount of the sample taken is determined by the loss in weight of the weighing bottle after distributing the sample over the pumice. The dish thus charged is placed in a vacuum oven in which a pressure not exceeding 5 ins. of mercury or a temperature not exceeding 70°C. is maintained. The vacuum oven devised by Carr (Browne's Handbook of Sugar Analysis, p. 20) is a convenient apparatus for this purpose.

For removal of the water from pure products, *e.g.* hydrated dextrose, raffinose, maltose, lactose, &c., the method devised by Lobry de Bruyn and Van Lænt (Rec. trav. chim. 38, 218) may be used. This method was employed by Brown, Morris and Millar (Chem. Soc. Trans. 71, 76) in their work on the products of starch hydrolysis by diastase. Briefly it is carried out as follows: Two small flasks are united by a tube furnished with a stop-cock and a side-tube leading to an air pump. The substance to be dehydrated is introduced into one of the flasks, the other being partially filled with phosphorus pentoxide. After exhausting the apparatus, the flask containing the substance is immersed in a water, salt water, or oil bath according to the final temperature required, and is slowly heated up to a point at which it ceases to lose weight.

Since in the estimation of water in the liquid or semi-liquid products above referred to,

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[1] This temperature was prescribed by the International Commission on the Unification of Methods of Sugar Analysis (Paris, 1900).

comparative rather than absolute accuracy is required, and expedition being an essential, indirect methods of estimating the solid matter (the amount of which is complementary to the water content) are usually resorted to. Two principles are made use of in these indirect methods, one depending on the specific gravities and the other on the refractive indices of sugar solutions. The specific gravities and refractive indices of sugar solutions are both functions of the solid matter present. In most tables, however, the assumption is made that the effect of all sugars is identical on specific gravity and refractive index, which, as will be seen, is not strictly accurate. The two principles will now be discussed seriatim.

Specific gravity method of estimating water and solid matter. A vast amount of labour has been devoted to the determination of the specific gravity of sucrose solutions. In 1854, Balling (Zeits. Ver. Rubenzuckerind. 4, 304) published his well-known tables giving the specific gravities of sucrose solutions of different concentrations.[1] His tables, which have since been extended by Brix, are now almost universally used on the Continent for determining the density of sugar solutions by means of a spindle. Another table was published by Gerlach in 1863, and this was subsequently recalculated to another temperature by Scheibler. The condensed table (XXVI.) taken from Browne's Handbook, p. 29, shows the relation between the results obtained by different authorities.

TABLE XXVI.—*Specific Gravity of Sucrose Solutions by Different Authorities.*

Sucrose, p.c. by weight	Balling-brix, $d\frac{17{\cdot}5^\circ}{17{\cdot}5^\circ}$C.	Gerlach, $d\frac{17{\cdot}5^\circ}{17{\cdot}5^\circ}$C.	Gerlach-Scheibler $d\frac{15^\circ}{15^\circ}$C.	German Imperial Commission	
				$d\frac{15^\circ}{15^\circ}$C.	$d\frac{20^\circ}{4^\circ}$C.
0	1·00000	1·00000	1·00000	1·00000	0·99823
5	1·01970	1·01969	1·01978	1·01973	1·01785
10	1·04014	1·04010	1·04027	1·04016	1·03814
15	1·06133	1·06128	1·06152	1·06134	1·05917
20	1·08329	1·08323	1·08354	1·08328	1·08096
25	1·10607	1·10600	1·10635	1·10604	1·10356
30	1·12967	1·12959	1·12999	1·12962	1·12698
35	1·15411	1·15408	1·15448	1·15407	1·15128
40	1·17943	1·17936	1·17985	1·17940	1·17645
45	1·20565	1·20559	1·20611	1·20565	1·20254
50	1·23278	1·23275	1·23330	1·23281	1·22957
55	1·26086	1·26086	1·26144	1·26091	1·25754
60	1·28989	1·28995	1·29056	1·28997	1·28646
65	1·31989	1·32005	1·32067	1·31997	1·31633
70	1·35088	1·35117	1·35182	1·35094	1·34717
75	1·38287	1·38334	1·38401	1·38286	1·37897

Another table which forms the basis of a hydrometer scale very widely used in the sugar and other industries is that of Beaumé. This table is based on the specific gravity of solutions of common salt. Table XXVII., abridged from that given in Browne's Handbook, shows the relation between the various scales. It will be observed that two Beaumé scales are given, the new and the old. The latter, although known to be inaccurate, is still retained in many countries.

TABLE XXVII.—*Specific Gavity of Sucrose Solutions at 17·5/17·5C. with Corresponding Degrees Brix and Baumé.*

P.c. sucrose by weight or degrees Brix	Specific gravity	Degrees Baumé	
		New	Old
1·0	1·00388	0·6	0·55
2·0	1·00779	1·1	1·1
3·0	1·01173	1·7	1·7
4·0	1·01570	2·3	2·2
5·0	1·01970	2·8	2·8
6·0	1·02373	3·4	3·3
7·0	1·02779	4·0	3·9
8·0	1·03187	4·5	4·4
9·0	1·03599	5·1	5·0
10·0	1·04014	5·7	5·55
11·0	1·04431	6·2	6·1
12·0	1·04852	6·8	6·7
13·0	1·05276	7·4	7·2
14·0	1·05703	7·9	7·8
15·0	1·06133	8·5	8·3
16·0	1·06566	9·0	8·9
17·0	1·07002	9·6	9·4
18·0	1·07441	10·1	10·0
19·0	1·07884	10·7	10·5
20·0	1·08329	11·3	11·1
21·0	1·08778	11·8	11·6
22·0	1·09231	12·4	12·2
23·0	1·09686	13·0	12·7
24·0	1·10145	13·5	13·3
25·0	1·10607	14·1	13·8
26·0	1·11072	14·6	14·35
27·0	1·11541	15·2	14·9
28·0	1·12013	15·7	15·4
29·0	1·12488	16·3	16·0
30·0	1·12967	16·8	16·5
31·0	1·13449	17·4	17·1
32·0	1·13934	17·95	17·6
33·0	1·14423	18·5	18·15
34·0	1·14915	19·05	18·7
35·0	1·15411	19·6	19·2
36·0	1·15911	20·1	19·8
37·0	1·16413	20·7	20·3
38·0	1·16920	21·2	20·8
39·0	1·17430	21·8	21·4
40·0	1·17943	22·3	21·9
41·0	1·18460	22·9	22·4
42·0	1·18981	23·4	23·0
43·0	1·19505	23·95	23·5
44·0	1·20033	24·5	24·0
45·0	1·20565	25·0	24·6
46·0	1·21100	25·6	25·1
47·0	1·21639	26·1	25·6
48·0	1·22182	26·6	26·1
49·0	1·22728	27·2	26·7
50·0	1·23278	27·7	27·2
51·0	1·23832	28·2	27·7
52·0	1·24390	28·8	28·2
53·0	1·24951	29·3	28·75
54·0	1·25517	29·8	29·3
55·0	1·26086	30·4	29·8
56·0	1·26658	30·9	30·3
57·0	1·27235	31·4	30·8
58·0	1·27816	31·9	31·3
59·0	1·28400	32·5	31·85
60·0	1·28989	33·0	32·4
61·0	1·29581	33·5	32·9
62·0	1·30177	34·0	33·4
63·0	1·30777	34·5	33·9
64·0	1·31381	35·1	34·4
65·0	1·31989	35·6	34·9
66·0	1·32601	36·1	35·4
67·0	1·33217	36·6	35·9
68·0	1·33836	37·1	36·4
69·0	1·34460	37·6	36·9
70·0	1·35088	38·1	37·4
71·0	1·35720	38·6	37·9
72·0	1·36355	39·1	38·4
73·0	1·36995	39·6	38·9
74·0	1·37639	40·1	39·4
75·0	1·38287	40·6	39·9

Table XXVIII. is for correcting readings of the Brix hydrometer, taken at different temperatures, to 17·5°C.

In his studies on the products of the hydrolysis of starch, O'Sullivan made use of a divisor for calculating the concentration (grms. per 100 c.c.) from the specific gravity of the solutions. This divisor was the excess specific gravity of a solution of maltose containing 10 grms. in 100 c.c. Brown and Heron subsequently suggested the divisor 3·86, which is the excess specific gravity (calling water 1000) of a solution containing 10 grms. of sucrose in 100 c.c. Comparative accuracy can be obtained with the use of this divisor with solutions containing up to 10 grms. per 100 c.c. of dissolved substance if the specific gravity is corrected for the influence of mineral matter (see below). If the specific gravities of the solutions are expressed in comparison with water as 1000, then obviously the values also express the weights in grams of 1 litre of the solution, or where the specific gravities are taken at 15·5°/15·5° or at any other temperature, the weight in grams of 1000 fluid grms. of the solution. It follows from this that the concentration (grams per 100 c.c.—100 fluid grms.) can be calculated by the aid of the

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[1] It should be pointed out that the solutions used by Balling were standardised on their true percentage of sucrose by weight and not grams per 100 c.c.

TABLE XXVIII.

Temperature, degrees Centigrade	Degrees Brix of solution												
	0	5	10	15	20	25	30	35	40	50	60	70	75
	Corrections to be subtracted from degrees Brix												
0°	0·17	0·30	0·41	0·52	0·62	0·72	0·82	0·92	0·98	1·11	1·22	1·25	1·29
5	0·23	0·30	0·37	0·44	0·52	0·59	0·65	0·72	0·75	0·80	0·88	0·91	0·94
10	0·20	0·26	0·29	0·33	0·36	0·39	0·42	0·45	0·48	0·50	0·54	0·58	0·61
11	0·18	0·23	0·26	0·28	0·31	0·34	0·36	0·39	0·41	0·43	0·47	0·50	0·53
12	0·16	0·20	0·22	0·24	0·26	0·29	0·31	0·33	0·34	0·36	0·40	0·42	0·46
13	0·14	0·18	0·19	0·21	0·22	0·24	0·26	0·27	0·28	0·29	0·33	0·35	0·39
14	0·12	0·15	0·16	0·17	0·18	0·19	0·21	0·22	0·22	0·23	0·26	0·28	0·32
15	0·09	0·11	0·12	0·14	0·14	0·15	0·16	0·17	0·16	0·17	0·19	0·21	0·25
16	0·06	0·07	0·08	0·09	0·10	0·10	0·11	0·12	0·12	0·12	0·14	0·16	0·18
17	0·02	0·02	0·03	0·03	0·03	0·04	0·04	0·04	0·04	0·04	0·05	0·05	0·06
	Corrections to be added to degrees Brix												
18	0·02	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·02
19	0·06	0·08	0·08	0·09	0·09	0·10	0·10	0·10	0·10	0·10	0·10	0·08	0·06
20	0·11	0·14	0·15	0·17	0·17	0·18	0·18	0·18	0·19	0·19	0·18	0·15	0·11
21	0·16	0·20	0·22	0·24	0·24	0·25	0·25	0·25	0·26	0·26	0·25	0·22	0·18
22	0·21	0·26	0·29	0·31	0·31	0·32	0·32	0·32	0·33	0·34	0·32	0·29	0·25
23	0·27	0·32	0·35	0·37	0·38	0·39	0·39	0·39	0·40	0·42	0·39	0·36	0·33
24	0·32	0·38	0·41	0·43	0·44	0·46	0·46	0·47	0·47	0·50	0·46	0·43	0·40
25	0·37	0·44	0·47	0·49	0·51	0·53	0·54	0·55	0·55	0·58	0·54	0·51	0·48
26	0·43	0·50	0·54	0·56	0·58	0·60	0·61	0·62	0·62	0·66	0·62	0·58	0·55
27	0·49	0·57	0·61	0·63	0·65	0·68	0·68	0·69	0·70	0·74	0·70	0·65	0·62
28	0·56	0·64	0·68	0·70	0·72	0·76	0·76	0·78	0·78	0·82	0·78	0·72	0·70
29	0·63	0·71	0·75	0·78	0·79	0·84	0·84	0·86	0·86	0·90	0·86	0·80	0·78
30	0·70	0·78	0·82	0·87	0·87	0·92	0·92	0·94	0·94	0·98	0·94	0·88	0·86
35	1·10	1·17	1·22	1·24	1·30	1·32	1·33	1·35	1·36	1·39	1·34	1·27	1·25
40	1·50	1·61	1·67	1·71	1·73	1·79	1·79	1·80	1·82	1·83	1·78	1·69	1·65
50	—	2·65	2·71	2·74	2·78	2·80	2·80	2·80	2·80	2·79	2·70	2·56	2·51
60	—	3·87	3·88	3·88	3·88	3·88	3·88	3·88	3·90	3·82	3·70	3·43	3·41
70	—	5·17	5·18	5·20	5·14	5·13	5·10	5·08	5·06	4·90	4·72	4·47	4·35
80	—	—	6·62	6·59	6·54	6·46	6·38	6·30	6·26	6·06	5·82	5·50	5·33
90	—	—	8·26	8·16	8·06	7·97	7·83	7·71	7·58	7·30	6·96	6·58	6·37
100	—	—	10·01	9·87	9·72	9·56	9·39	9·21	9·03	8·64	8·22	7·76	7·42

formula $C = \frac{S-1000}{d}$, where C is the required concentration, S is the specific gravity of the solution, and *d* the excess specific gravity of a 1 p.c. solution of any given pure sugar.

Brown, Morris and Millar (Chem. Soc. Trans. 71, 72) have determined the divisors for sucrose, dextrose, fructose, invert sugar, maltose and certain mixed products of the hydrolysis of starch at various concentrations. Ling, Eynon and Lane (Seventh Inter. Cong. Appl. Chem., Section I., p. 137) have repeated this work for solutions of dextrose, lævulose and maltose. The following may be regarded as the accurate divisors for solutions for the undermentioned sugars containing 10 grms. in 100 c.c. Sucrose, 3·86 (Brown and Heron), dextrose, 3·82 (Ling, Eynon and Lane), lævulose, 3·92 (Ling, Eynon and Lane), invert sugar, 3·87 (mean of dextrose and lævulose values), maltose, 3·91 (Ling, Eynon and Lane). Mixed starch transformation products 3·93–4·01 (Brown, Morris and Millar). The divisor in all cases increases with a decrease of concentration. In the analysis of commercial products, however, solutions containing 10 grms. per 100 c.c. are usually employed. It has already been mentioned that in applying this method of estimating the concentration of a sugar solution, it is necessary to correct for the influence of the mineral matter. Solutions of most salts have much higher specific gravities for a given concentration than those of the sugars. Heron found that the mean specific gravity of a solution of the sulphated mineral matter containing 1 grm. per 100 c.c. is 1008, and this value in the writer's experience is not far from the truth. If, therefore, the percentage of soluble ash in a sample be multiplied by 0·8 and the product deducted from the specific gravity of the solution of c=10, the remainder divided by the appropriate number will give the grams of sugar per 100 c.c. with a fair degree of accuracy. Proteins have very little influence on this method, as the specific gravities of their solutions are so low. To calculate the carbohydrate concentration of beer worts, the writer, after diluting to a specific gravity of about 1040, determines the specific gravity at 15·5°/15·5°, corrects for ash as above and divides the corrected excess specific gravity by 4. This practice is also adopted by several other chemists.

Refractometric methods of estimating water and solid matter. The principle and construction of different forms of the refractometer is dealt with in a special article (vol. iv. p. 550). These instruments have been applied to a large number of products for several years, but the

TABLE XXIX.—*Refractive Index and Water Content of Sugar Solutions.*

$n_D^{20°}$	w	$n_D^{20°}$	w
1·3330	100	1·3883	66
1·3344	99	1·3902	65
1·3359	98	1·3920	64
1·3374	97	1·3939	63
1·3388	96	1·3958	62
1·3403	95	1·3978	61
1·3418	94	1·3997	60
1·3433	93	1·4016	59
1·3448	92	1·4036	58
1·3464	91	1·4056	57
1·3479	90	1·4076	56
1·3494	89	1·4096	55
1·3510	88	1·4117	54
1·3526	87	1·4137	53
1·3541	86	1·4158	52
1·3557	85	1·4179	51
1·3573	84	1·4200	50
1·3590	83	1·4221	49
1·3606	82	1·4242	48
1·3622	81	1·4264	47
1·3639	80	1·4285	46
1·3655	79	1·4307	45
1·3672	78	1·4329	44
1·3689	77	1·4351	43
1·3706	76	1·4373	42
1·3723	75	1·4396	41
1·3740	74	1·4418	40
1·3758	73	1·4441	39
1·3775	72	1·4464	38
1·3793	71	1·4486	37
1·3811	70	1·4509	36
1·3829	69	1·4532	35
1·3847	68	1·4555	34
1·3865	67		

first to suggest their application to commercial sugars and molasses was apparently Stromer in 1883 (Oest. Ung. Zeit. Zuckerind. 12, 925; 13, 185), who pointed out that the refractive indices and specific gravities of sugar solutions ran parallel to one another. In 1901, Stolle (Zeits. Ver. Deuts. Zuckerind. 51, 469) showed that solutions of sucrose, dextrose, lævulose, and lactose of the same concentration had substantially the same refractive indices. He used the Pulfrich instrument. The next work of importance in this connection is that of Tolmann and Smith (J. Amer. Chem. Soc. 28, 1476), who used an Abbe refractometer. The first to place the refractometric method on a sound practical basis, as regards its application to sugar analysis, was, however, Main (Inter. Sugar Journ. 9, 481). Main worked with the Abbe refractometer and constructed a table which has since been checked by Schönrock in the laboratories of the Physikalisch-Technische Reichanstalt, Berlin. Schönrock's [1] results, which are given in Table XXIX., show no greater deviation from those of Main than 4 in the fourth place of decimals.

Stanek (Zeits. Ver. Deutsch. Zuckerind. 61, 421) determined the corrections to be applied to Main's table, when the observations are made at temperatures other than 20°C. His results are embodied in Table XXX.

The immersion refractometer (*l.c.*, vol. iv. p. 553) has also been employed for sugar products. The range is, however, much less than that of the Abbe instrument, the scale being restricted to solutions containing 21·7 p.c. of sugar and less. The instrument is, however, capable of yielding

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[1] Schönrock has modified the Abbe refractometer. Instead of glass of refractive index of 1·7 he uses the less refractive flint glass. This enables darker products and more concentrated solutions—up to 85 per cent. concentration—to be examined. The modified instrument is constructed by Messrs. Zeiss & Co.

TABLE XXX.—*Stanek's Correction Table.*

For Determining Water in Sugar Solutions by means of the Abbe Refractometer when Readings are made at other Temperatures than 20° C.

Water per cent.	95	90	85	80	70	60	50	40	30	25	Water per cent.
Temperature C.	To be added to the per cent. of water.										Temperature C.
15	0·25	0·27	0·31	0·31	0·34	0·35	0·36	0·37	0·36	0·36	15
16	0·21	0·23	0·26	0·27	0·29	0·31	0·31	0·32	0·31	0·29	16
17	0·16	0·18	0·20	0·20	0·22	0·23	0·23	0·23	0·20	0·17	17
18	0·11	0·12	0·14	0·14	0·15	0·16	0·16	0·15	0·12	0·90	18
19	0·06	0·07	0·08	0·08	0·08	0·09	0·09	0·08	0·07	0·05	19
	To be subtracted from the per cent. of water.										
21	0·06	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07	21
22	0·12	0·14	0·14	0·14	0·14	0·14	0·15	0·14	0·14	0·14	22
23	0·18	0·20	0·20	0·21	0·21	0·21	0·23	0·21	0·22	0·22	23
24	0·24	0·26	0·26	0·27	0·28	0·28	0·30	0·28	0·29	0·29	24
25	0·30	0·32	0·32	0·34	0·36	0·36	0·38	0·36	0·36	0·37	25
26	0·36	0·39	0·39	0·41	0·43	0·43	0·46	0·44	0·43	0·44	26
27	0·43	0·46	0·46	0·48	0·50	0·51	0·55	0·62	0·50	0·51	27
28	0·50	0·53	0·53	0·55	0·58	0·59	0·63	0·70	0·57	0·59	28
29	0·57	0·60	0·61	0·62	0·66	0·67	0·71	0·78	0·65	0·67	29
30	0·64	0·67	0·70	0·71	0·74	0·75	0·80	0·86	0·73	0·75	30
Water per cent.	95	90	85	80	70	60	50	40	30	25	Water per cent.

more accurate results than the Abbe refractometer, since it gives a much sharper border line than the latter.

Comparison of densimetric and refractometric methods. When either of these methods is applied to commercial products, the assumption is made that the results are affected similarly by all the solid matters present, which is by no means the case. It has been shown above, for example, that the divisors to be applied to the specific gravities of solutions of sugars in order to calculate their concentration, differ according to the particular sugar dealt with, and that they also vary with the concentration of the solution of one and the same sugar. Further, weight for weight mineral matter produces, roughly speaking, twice the effect on specific gravity as do sugars themselves, whilst protein substances have a much lower specific gravity coefficient than have the sugars. Refractometric methods, on the other hand, can be applied over a much wider range of mixtures without impairing their accuracy for practical requirements, than can densimetric methods. Thus, Stanek, working with Main's table, has shown (Zeits. Zuckerind. Böhmen, 34, 5) that with solutions of betaine, sodium formate, potassium formate, sodium acetate, potassium acetate, sodium butyrate, sodium lactate and potassium lactate, a very fair approximation to the truth is obtained with refractometric methods, whilst with densimetric methods the divergencies from the truth are considerable. It should be pointed out, however, that whereas refractometric values can only be determined to four significant places, it is easy to measure specific gravities to five significant places.

The writer desires to thank his assistant, Mr. George McLaren, for help in collecting together some of the commercial analyses recorded in this article. A. R. L.

SUGAR CANE WAX *v.* WAXES.

SUGAR OF LEAD. *Lead acetate* (*v.* ACETIC ACID).

SUINE. A butter substitute made from pigs' fat (*v.* MARGARINE).

SULFAMINOL *v.* SYNTHETIC DRUGS.

SULFOSOT *v.* SYNTHETIC DRUGS.

SULPHAMMONIUM. The various forms of sulphur dissolve in liquid ammonia forming a purple solution, which, according to Moissan, contains a definite compound, stable up to 90°, which he terms *sulphammonium*. It gives a characteristic absorption spectrum and reacts with iodine and a number of metals and salts forming coloured substances decomposing at the ordinary temperature and pressure (Moissan, Bull. Soc. chim. 1902, [iii.] 27, 652).

SULPHANILIC ACID (p-*Aniline sulphonic acid*) $C_6H_4{\cdot}NH_2{\cdot}HSO_3$, or $C_6H_4<\genfrac{}{}{0pt}{}{SO_3}{NH_3}>$ is formed by heating aniline *p*-phenol sulphonate, or by heating aniline with concentrated sulphuric acid, or aniline ethyl sulphate to 200° (Limpricht, Annalen, 1875, 177, 80); the nitration products of benzene sulphonic acid, when reduced with ammonium hydroxide and hydrogen sulphide, yield the three aminosulphonic acids, which may be separated mechanically after recrystallisation. The light crystals of the *m*-acid rise to the surface, and may be removed from the others by washing. The residue is heated to 110°–120° when the *p*- acid becomes powdered and may be separated by passing through a sieve (Franklin, Amer. Chem. J. 1898, 20, 457).

Sulphanilic acid may be prepared by heating 28 parts of chlorobenzene-*p*-sulphonic acid with 370 of 25 p.c. ammonia solution, and 5 of cupric chloride for 12 hours to 170° in a closed vessel. The mass is then mixed with sodium carbonate, the ammonia is distilled off, the residue filtered and concentrated, when the sodium salt of sulphanilic acid separates (Bloxam, D. R. P. 205150; J. Soc. Chem. Ind. 1908, 1147). The acid may also be obtained by the action of hot strong acids or alkalis on acetylaniline-*p*-sulphonamide (Gelmo, J. pr. Chem. 1908, [ii.] 77, 369), and by other methods (Gerhardt, Annalen, 1846, 60, 310; Buckton and Hofmann, *ibid.* 1856, 100, 163; Pratesi, Ber. 1871, 4, 970; Kopp, *ibid.* 978; Bamberger and Kunz, *ibid.* 1897, 30, 2277; Wenghöffer, J. pr. Chem. 1877, [ii.] 16, 454; Wohlfahrt, *ibid.* 1902, 66, 551; Cohn and Springer, Monatsh. 1903, 24, 87; Bouchetal, Bull. Soc. chim. 1904, [iii.] 31, 24).

Sulphanilic acid forms a monohydrate and a dihydrate. The stable solid in contact with saturated solutions is dihydrate from 0° to 21°. monohydrate from 21° to 40°, and anhydrous acid from 40° upwards (Philip, Chem. Soc. Trans. 1913, 284). The dihydrate is strongly efflorescent, and on losing its water at the ordinary temperature, passes directly into the anhydrous acid. The latter may be obtained by crystallisation not only from hot water, but also from fuming sulphuric acid (Laar, Ber. 1881, 14, 1933). It chars when heated to 280°–300°. It acts as a monobasic acid (Astruc, Compt. rend. 1900, 130, 1563), yields aniline when fused with caustic potash, and when the barium salt is treated with bromine water, it forms tribromaniline and barium dibromoanilinesulphonate. When oxidised with chromic acid it yields quinone (Schrader, Ber. 1875, 8, 759; Limpricht, *ibid.* 1885, 18, 1419; Laar, J. pr. Chem. 1879, [ii.] 20, 242).

Sulphanilic acid forms salts with the alkali metals, also with barium copper, silver, and cerium (Gerhardt, *l.c.*; Laar, *l.c.*; Morgan and Cahen, Chem. Soc. Trans. 1907, 477). On pouring a mixture of sodium sulphanilate and sodium nitrite in aqueous solution into dilute sulphuric acid, it forms *benzene-diazonium sulphonic acid* $C_6H_4<\genfrac{}{}{0pt}{}{N_2}{SO_3}>$, which is important in the preparation of azo dyes, such as helianthine. Finely powdered dry sodium sulphanilate reacts with acetic anhydride forming *sodium acetylaniline*-p-*sulphonate*, which, with concentrated sulphuric acid, yields the free acid $NHAc{\cdot}C_6H_4{,}SO_3H$. The sodium acetyl salt treated with phosphorus pentachloride and then with cold water yields the corresponding *sulphonyl chloride* $NHAc{\cdot}C_6H_4{,}SO_2Cl$, m.p. 149° (Schroeter, Ber. 1906, 39, 1559).

When 46·2 grms. of sodium -*p*-sulphanilate is heated with 1 litre of water, 18 c.c. hydrochloric acid, and 54 grms. of tetramethyldiaminodiphenylcarbinol, on a water-bath for 6 hours to 80°–90°, equal quantities of the following substances are obtained: (1) a yellow crystalline compound dyeing tannin-mordanted cotton yellow, similar to auramine; (2) a sulphonated leuco base, converted by lead peroxide into a green dyestuff for wool, decolorised by alkalis; (3) a substance soluble in water, which does not yield a dyestuff on oxidation; (4) hexamethyltriaminotriphenylmethane (crystal violet). With *m*-sulphanilic acid treated similarly (but in different proportions), yields as chief product a sulphonated leuco base, which, on oxidation, yields a violet dyestuff turned green by caustic soda. If the leuco base is diazotised, boiled with water, and then oxidised, it yields a green dyestuff, reddened by alkalis; but if the diazo compound is boiled with alcohol and the product oxidised with lead peroxide, it forms a dyestuff which colours wool bluish-green shades remarkably fast to caustic soda (Suais, Bull. Soc. chim. 1897, [iii.] 17, 517).

Sulphanilic acid yields a number of nitro, halogen, and other derivatives.

SULPHAZIDES may be prepared by the action of sulphurous acid upon the acid solution of diazo salts, or by passing nitrous acid into or adding potassium nitrite to, an ice-cooled solution of the diazo salt in alcohol saturated with sulphurous acid (Limpricht, Ber. 1887, 20, 1238). According to Eng. Pat. 12872, 1900, a much better yield is obtained by diazotising an aromatic amine in hydrochloric acid solution, mixing this with sodium bisulphite and adding the diazo sulphite thus formed to an alcoholic solution of sulphurous acid (J. Soc. Chem. Ind. 1900, 893).

Phenylbenzenesulphazide

$$C_6H_5NH{\cdot}NHSO_2C_6H_5$$

forms white leaflets, m.p. 148°–150°.

***o*-Tolyltoluenesulphazide**

$$C_7H_7NH{\cdot}NHSO_2C_7H_7$$

forms white lustrous needles, m.p. 140°–142° (decomp.); the *p*-tolyl- derivative has m.p. 140°.

Nitro derivatives of these compounds are described by Limpricht (*l.c.*).

When the sulphazides are heated with baryta, or with soda solution, or with alcoholic soda, they are decomposed, yielding the corresponding sulphinic acid, nitrogen, and an aromatic hydrocarbon.

Similarly, nitrosulphinic acids and nitrohydrocarbons are formed from the nitrosulphazides.

SULPHIDE DYES.

Historical summary. Sulphur enters into the composition of many important organic colouring matters of widely different properties and mode of application (*v.* METHYLENE BLUE, PRIMULINE, &c.), but the group of dyes comprised under the above heading is distinguished by the dyeing process employed in fixing these compounds on the textile fibres, usually cotton. The sulphide dyes are soluble with reduction in aqueous solutions of the alkali sulphides giving rise to leuco derivatives which have a considerable affinity for the cotton fibre. After absorption by the cotton these leuco compounds are oxidised *in situ* to the insoluble dye, either by air or by chemical agents. In this behaviour the sulphide colours somewhat resemble indigotin, thioindigo, and other vat dyes (*v.* VAT DYES, &c.), and proposals have been made for employing these colours in the vat-dyeing processes (D. R. PP. 146797, 200391).

The earliest experiments in this field of tinctorial chemistry were made by Troost in 1861, who reduced a crude mixture of 1 : 5- and 1 : 8-dinitronaphthalenes with sodium sulphide and other reducing agents, and obtained coloured products giving red, violet, and blue shades on the textile fibres (J. 1861, 958; *cf.* Fr. Pat. 244885). But although these experiments indicated the influence of sulphur in the conversion of organic compounds into colouring matters, the substances produced met with no success as dyes. The first discovery of technical importance was embodied in a patent taken out by Croissant and Bretonnière (Eng. Pat. 1489, 1873; Fr. Pat. 98915; *cf.* Bull. Soc. Ind. Mulhouse, 1874, 468), in which these chemists showed that a very heterogeneous collection of organic materials were capable of yielding dyes when heated with alkali sulphides and polysulphides. The materials enumerated in the patent are in most cases products of the vital activities of animal and vegetable life, together with certain waste products of manufacture, among which the following may be mentioned: wood, sawdust, humus, vegetable detritus, lichens, mosses, bran, farina, glutin, starch, sucrose, glucose, cellulose, paper and cotton waste, tannin, gallic acid, gelatin, casein, albumin, blood, horn, feathers, animal excrement, the organic acids and their salts, aloes, resins, gums, gum-resins, and soot.

Two modes of interaction are distinguishable in the patent. In one process aloes are warmed with an aqueous solution of sodium polysulphide when a dye is produced, dyeing cotton in lilac and grey shades. The patentees state that this dye is an additive product, the sulphur being introduced into the molecule without replacement of hydrogen in the form of hydrogen sulphide.

In the second process, which is by far the more widely applicable, the organic matter is heated with alkali polysulphides at temperatures above 100° and approaching 300°. Substitution occurs, sulphur being introduced into the molecule while hydrogen sulphide is evolved. The products dye in various shades of brown, and the patentees' experiments indicated that the higher the temperature of heating the darker was the shade of colour produced.

In spite of the wide scope of the patent only one useful colour was obtained under it for about 20 years. This product was **Cachou de Laval**, a brown dye which was generally prepared by heating together sawdust, sodium sulphide, and sulphur (*v. infra*).

The next development in the sulphide dye industry occurred 20 years later, when Vidal found that certain aromatic nitro compounds were capable of yielding green, blue, brown, and even black dyes (**Vidal black**) when heated with alkali polysulphides. This discovery was the turning-point in the manufacture of sulphide colours, for from this time onward the attention of inventors was directed towards the production of these colours from definite coal-tar derivatives rather than from the ill-defined materials indicated in Croissant and Bretonnière's patent.

The compounds first utilised by Vidal for the production of brown and black sulphur dyes were the nitrated products of phenol and its homologues. Acyl derivatives of aromatic nitro-amines and diamines were then employed (D. R. P. 82748), and in 1897 the nitro derivatives of hydroxydiphenylamine were made use of in the production of **Immedial black.** Improvements in the manufacture of sulphide blues speedily followed, culminating in the discovery in 1900 of **Immedial pure blue** and its homologues from dialkyl-*p*-amino-*p*-hydroxydiphenylamines (D. R. P. 134947).

The addition of copper salts, or even finely-divided copper to the alkali sulphide fusions of diamino- and dialkylamino-hydroxydiphenylamines led in 1901 to the production of green sulphide dyes (D. R. PP. 135410, 148024).

Yellow, orange, and brown sulphide dyes resulted in 1902 from the thionation of tolylene-2:4-diamine and its acyl derivatives with sulphur alone, the products being rendered soluble by subsequent treatment with aqueous sodium sulphide (D. R. PP. 139430, 144762 152595). These dyes resemble the thiazole colouring matters in the fact that they are formed from aromatic compounds containing methyl and other non-aromatic groups. These side chains play an essential part in the production of the colouring matter, just as they do in the case of dehydrothiotoluidine and primuline, for diamines, such as *m*-phenylenediamine, without side chains do not furnish these yellow and orange dyes.

Although the problem of producing scarlet and bright-red sulphide dyes has not hitherto been solved, it has been shown that colouring matters of distinctly reddish shade can be obtained by thionating certain of the red dyestuffs, such as the azines, rosindulines, and safranines, in some cases in the presence of copper salts (D. R. PP. 126175, 152373, 161462, 177709, 181125).

These red sulphide dyes, however, are less fast to light than the brown and black dyes of this series, and the yellow sulphide colours also suffer to some extent from this drawback. On this account the greatest development of the sulphide dye industry has taken place in the production of brown, blue, and particularly black dyes, the last of which are now manufactured on an enormous scale owing to their cheapness, fastness, and ease of application.

As the exact chemical constitution of the various commercial sulphide dyes is not in general known with certainty, it will be convenient to group these substances together in accordance with their tinctorial properties.

The firms engaged in the manufacture of sulphide dyes designate their respective products by generic names which are set forth in the following table; the abbreviations in brackets are used throughout this article to indicate the makers or patentees of the various products described.

Manufacturers.	*Sulphide dyes.*
Aktiengesellschaft für Anilin Fabrikation, Berlin (*A.*)	Sulphur colours.
Badische Anilin-Soda-Fabrik, Ludwigshafen a/Rhein (*B.*)	Kryogen „
Gesellschaft für Chemische Industrie in Basel (*Bl.*)	Pyrogen „
Farbenfabriken vorm. Fr. Bayer & Co., Elberfeld (*By.*)	Katigen „
Leopold Cassella & Co., Frankfurt a/Main (*C.*)	Immedial „
Carl Jäger, Düsseldorf-Derendorf (*C. J.*)	Thiophor Indigo, &c.
Clayton Aniline Co., Ltd., Clayton, Manchester (*Cl. Co.*)	Clayton black, &c. [browns, &c.
Dahl & Co., Barmen (*D.*) . .	Cotton blacks,
Anilinfarben und Extrakt-fabriken vorm. J. R. Geigy (*G.*)	Eclipse colours.
Read Holliday & Sons, Ltd., Huddersfield (*H.*)	Cross dye colours.
Kalle & Co., Biebrich a/Rhein (*K.*)	Thion colours.
Farbwerk Mülheim vorm. A. Leonhardt & Co., Mülheim bei Frankfurt (*L.*)	Pyrol black, &c.
Levinstein, Ltd., Blackley, Manchester (*Lev.*)	Thionol colours.
Farbwerke vorm. Meister, Lucius & Brüning, Höchst a/Main (*M.*)	Thiogene colours, melanogen blue, &c.
Chemische Fabrik Griesheim-Elektron, Werk Oehler (vorm. K. Oehler, Griesheim) (*O.*)	Thioxine colours.
Société Anonyme des Matières Colorantes et Produits Chemiques de St. Denis, Paris (*P.*)	Vidal black, thiocatechine.
Chemische Fabriken vorm. Weiler ter Meer, Uerdingen a/Rhein (*T. M.*)	Auronal black, &c.
Sandoz & Co. (vorm. Kern & Sandoz), Basle (*K. S.*)	Thional colours.

BLACK SULPHIDE DYES.

Vidal black (*P.* Eng. Pats. 23578, 1893; 9943, 1894; D. R. PP. 85330, 90369) is produced by heating with alkali polysulphides either *p*-aminophenol or substances capable of yielding this compound. *p*-Nitrophenol (100 parts) is slowly added to 400 parts of crystallised sodium sulphide, $Na_2S,9H_2O$, melted in its water of crystallisation; the temperature is raised to 130°, and, when reduction is complete, 75 parts of sulphur are introduced and the mixture heated to 150°–175°. A vigorous reaction takes place, hydrogen sulphide being evolved freely; finally the mixture becomes too solid to be stirred, and is dried at 180° until quite hard and crisp. The dried mass can then be used directly in dyeing, or the dye may be purified by precipitation from aqueous sodium sulphide with dilute hydrochloric acid. Its solution in alkali sulphide is green, and cotton is dyed in green shades which change to black when the fabric is subsequently chromed, the black shades thus produced are extremely fast to light and scouring agents.

Vidal black is a black mass with bronzy reflex, and its green leuco derivative, produced by aqueous sodium sulphide, can be further changed by powerful reducing agents (zinc and sodium hydroxide) to a reduction product having no affinity for cotton.

The purified dye is obtained by dissolving the crude fusion product in water and precipitating with dilute acetic or hydrochloric acid. The precipitate when washed free from inorganic salts is dried at 110°, extracted with carbon disulphide till free from uncombined sulphur, washed with dry ether and light petroleum, and dried at 90°–100°. The product is thus obtained in small amorphous black nodules with dark bronzy lustre; it contains about 32 p.c. of combined sulphur.

Vidal black S (D. R. P. 88392) is the soluble sulphite compound of the preceding dye produced by adding 100 kilos. of 15 p.c. Vidal black paste to an aqueous solution containing 50 kilos. of sodium sulphite or bisulphite.

A modified Vidal black is obtained by heating with sulphur at 240° *p*-aminophenol and its homologues with acetanilide, the acetotoluidides, &c. (*G.* D. R. P. 128361).

Clayton black D (*Cl. Co.* D. R. P. 106030;

Eng. Pat. 21832, 1898). Nitrosophenol (95 parts), is dissolved in 92 parts of sodium hydroxide (38°Be.), diluted with 500 parts of water and mixed successively with 500 parts of sodium thiosulphate in 300 parts of water and 750 parts of 30–40 p.c. sulphuric acid below 22°. The filtered solution mixed with an alkaline solution of 57 parts of nitrosophenol is heated for 4–6 hours until sulphur dioxide is all evolved, and then cooled, when the precipitated dyestuff is collected.

Clayton black D. is soluble in aqueous sodium hydroxide or carbonate to a coal-black solution turned violet by sodium sulphite; it dissolves in concentrated sulphuric acid to a blue solution and when dyed on cotton in sodium sulphide bath, 10 p.c. of colour gives an intense pure black, which is deepened by chromic acid or copper sulphate, and is fast to acids, alkalis, and soap.

Dinitrophenol black; immedial black N; sulphur black T extra; thiophenol black T extra; thionol black; cross dye black B X (D. R. PP. 127835, 136016, 218517; Eng. Pats. 19831, 1896; 13035, 17805, 1903; Fr. Pats. 259509, 267343, 333096). Thirty parts of 2:4-dinitrophenol are slowly added to a solution of 125 parts of sodium sulphide $Na_2S,9H_2O$, and 45 parts of sulphur in 150 parts of water, and the mixture boiled under a reflux apparatus (103°–106°) for 25–40 hours. The boiling mass, which assumes a green colour changing to bluish-black, is then poured into water, and the filtered solution is either acidified or oxidised by a current of air. The bluish-black colouring matter is collected and washed free from inorganic salts. The dye is further purified by dissolving in aqueous sodium sulphide, reprecipitating by filtered air and washing the precipitate until free from sodium salts. The product is then dried at 100°–110°, and extracted with boiling carbon disulphide until free from uncombined sulphur. Dinitrophenol black is thus obtained as a bluish-black bronzy mass devoid of crystalline structure. It dissolves in aqueous alkali sulphides to a dark greenish-blue solution, and is practically insoluble in cold concentrated sulphuric acid.

A specimen of cross dye black BX (*H.*), purified in the foregoing manner, contained 29·0 p.c. of sulphur and 12·5 p.c. of nitrogen. Thionol black O extra (*Lev.*) when similarly isolated, contained 28·0 p.c. of sulphur and 10·4 p.c. of nitrogen. Thionol black OO extra (*Lev.*) contained 36·0 p.c. of sulphur.

The great commercial importance of this colouring matter lies in the fact that it dyes unmordanted cotton in intense black shades which are fully developed by aerial oxidation without subsequent treatment with chromic acid or any other oxidising agent. Moreover, the colour is not affected in tint by after-chroming, and it is remarkably fast to light, acids, alkalis, and scouring and milling agents.

Immedial black NN. The above-described method for making dinitrophenol black is a boiling process carried out at comparatively low temperatures (103°–106°) in aqueous solution, and in this respect the result is an exception to the general tendency, noticed by Croissant and Bretonnière (*v. supra*), for darker shades to be produced at higher temperatures. Vidal, who first suggested the use of dinitrophenol for making sulphur blacks, devised a melting process which leads to products totally different from the black obtained by the boiling process and dyeing cotton in worthless dark-brown shades (Eng. Pat. 16449, 1896; D. R. P. 98437). When, however, the reagents are mixed in the following proportions, dinitrophenol (25 parts), sodium sulphide (125 parts), and sulphur (50 parts), and heated gradually to 160° and maintained at this temperature until the fusion becomes solid (2–3 hours), then a black is obtained, but a departure from these proportions, which correspond with Na_2S_5, leads to brown products (*C.* Eng. Pat. 19831, 1896). The product of fusion is dissolved in water and the dye precipitated by acid or air and made into a paste or dried.

Thion black (*K.*) is a similar product obtained by a melting process at 140°–160° for 2–3 hours, using 35 parts of sodium tetrasulphide and 20·6 parts of sodium dinitrophenoxide (Eng. Pat. 26379, 1903).

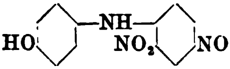
Thional black (*K. S.* Eng. Pat. 26465, 1901) is produced in aqueous solution under pressure at 160°–165° from dinitrophenol (92 parts) sodium thiosulphate (400 parts), 33 p.c. sodium hydroxide (61 parts), and water (800 parts).

Thiophenol black T extra (*Bl.* Eng. Pat. 13035, 1903) is obtained from dinitrophenol and polysulphide either at 115°–140° under the ordinary pressure, or at 110°–115° under a pressure of 2½ atmospheres, and a greener shade of black is produced either by adding copper salts or 5 p.c. of chloro-2:4-dinitrobenzene (*cf.* D. R. P. 208377; Eng. Pat. 27213, 1906).

The dinitrophenol employed in these operations is prepared by the action of boiling aqueous sodium hydroxide on chloro-2:4-dinitrobenzene, and the latter substance has itself been employed in the boiling process with sodium hydroxide and polysulphide when hydrolysis and thionation occur in one operation (Eng. Pat. 26345, 1904).

Cross dye black R X (*H.*) is produced from a mixture of 2:4-dinitrophenol and picric or picramic acid in the boiling process; it gives a redder shade of black than cross dye black B X, and dissolves slightly in cold concentrated sulphuric acid to a purple-blue solution. Picramic acid (14 parts), sodium sulphide (60 parts), and sulphur (25 parts) in 50 parts of water give after 24 hours' boiling under a reflux condenser a violet-black dye (*A.* Eng. Pat. 7332, 1900; D. R. P. 116791). The dinitrated products of the cresols and chlorophenols also yield various shades of sulphide blacks by the boiling process (*A.* Eng. Pats. 7076, 1900; 15625, 1909; D. R. P. 129564).

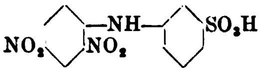
Immedial black V extra (*C.*). *p*-Aminophenol and chloro-2:4-dinitrobenzene, when boiled in alcoholic solution in the presence of sodium acetate, yield 2:4-dinitro-4′-hydroxydiphenylamine



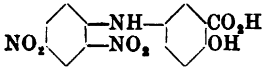
Fifteen parts of this substance are heated for 5 hours in a reflux apparatus with sodium sulphide crystals (75 parts), sulphur (30 parts), and a small amount of water to 140°–160°, the dye being precipitated from an aqueous solution of the fused product by acid, carbon dioxide, or air. Cotton is dyed in bluish-black shades, and when oxidised on the fibre with hydrogen peroxide the colour changes to blue (**Immedial blue,** *C.* D. R. P. 103861; Eng. Pat. 25234, 1907; Fr. Pat. 271909). The immedial black fusion may be carried out under pressure; the 2 : 4-dinitro-4′-hydroxydiphenylamine (10 parts) and dry sodium tetrasulphide (18 parts) are heated in an autoclave with 50–60 parts of alcohol, and the product, suspended in water, is converted into immedial blue by the addition of hydrogen peroxide (*C.* D. R. PP. 132424, 137784; Eng. Pat. 5385, 1900). The colour on cotton is fast to chlorine, light, and scouring agents.

When immedial black, eclipse black, or kryogen black is heated up to 200° with 1 : 8-dinitronaphthalene and sodium polysulphide, a black is produced which is more stable to oxidising agents than that from either of its generators (*v. Fast black, B.* Fr. Pat. 319790).

Cotton black (*D.* Eng. Pat. 13167, 1898; D. R. PP. 101862, 105058). Chloro-2 : 4-dinitrobenzene is condensed with 3-aminobenzenesulphonic acid and the resulting 2 : 4-dinitrodiphenylamine-3′-sulphonic acid (12 parts) is thionated with sodium sulphide (60 parts), sulphur (8 parts), and water (5 parts), the temperature being raised to 200°–220°. The colouring matter dyes in greenish-black shades which are not affected by oxidising agents. 2 : 4-Dinitrodiphenylamine-4′-sulphonic acid gives a coal-black sulphide dye absolutely fast to milling.

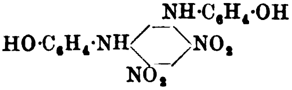


Sulphanil black C (*K.*). Chloro-2 : 4-dinitrobenzene is condensed with 4-aminosalicylic acid, the product, 2 : 4-dinitro-4′-hydroxydiphenylamine-3′-carboxylic acid is thionated at 150° with an equal weight of sulphur and 2·5 parts of sodium sulphide (D. R. P. 129885).



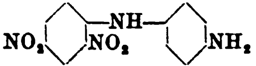
Katigen black (*By.*) is produced in a similar way by the thionation of 2 : 4-dinitro-2′-hydroxydiphenylamine-3′-carboxylic acid (D. R. P. 112182).

Kryogen blacks G, BG, B, N, result from the condensation of dinitro-*m*-dichlorobenzene with *p*-aminophenol (2 mols.), and its sulphonic and carboxylic acids, these three reagents on thionation giving respectively deep black, greenish-black, and bluish-black shades (*B.* Eng. Pat. 20232, 1899; D. R. P. 112298).



Indocarbon black S, SF (*C.*). The indophenol obtained by condensing carbazole (40 parts), nitrosophenol (30 parts) in 1100 parts of concentrated sulphuric acid at 15°, is heated with sodium sulphide, sulphur, aqueous sodium hydroxide, and copper sulphate in a reflux apparatus at 125° for 18 hours. The product, which is precipitated by air from sodium sulphide solution, gives full bluish-black shades very fast to chlorine (D. R. P. 221215). Similar dyes are produced from halogenated carbazoles and the homologues and substitution products of nitrosophenols (*v.* D. R. PP. 222640, 224590, 224591, 227323, 235364, 235836, 238857).

Auronal black (*T. M.*) is prepared from 2 : 4-dinitro-4′-aminodiphenylamine (36 parts) derived from chloro-2 : 4-dinitrobenzene and *p*-phenylenediamine by heating with sodium sulphide (180), sulphur (60), water (60), and glycerol (15 parts), the last substance serving to regulate the temperature of the boiling solution. At 165° a colour is produced, dyeing in dark-blue shades rendered faster by afterchroming. This product gives reddish-blue and violet solutions in concentrated sulphuric acid and aqueous sodium hydroxide respectively. At 170°–180° the fusion gives a bluish- or greenish-black, the colours in concentrated sulphuric acid being greenish-blue and black respectively. At 180° a spontaneous generation of heat occurs and an olive sulphide dye is produced (D. R. P. 144119; Eng. Pat. 11733, 1901).



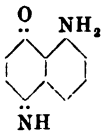
The above diphenylamine derivative is converted into a greenish-black compound by heating up to 150° with sodium polysulphide and hydroxide (*K.* D. R. P. 134704); in the absence of caustic alkali an insoluble product is obtained.

Pyrol black (*L.*). *p*-Aminophenol (11 kilos.) is heated with its hydrochloride (15 kilos.) for 10 hours at 170°, or for 5–6 hours at 180°–220°; 12 kilos. of the condensation product insoluble in dilute acids are heated at 180°–220° with 30 kilos. of sodium sulphide and 4 kilos. of sulphur. The fusion dissolves in water to a dark blue solution from which acids precipitate the black dye. The leuco compound with zinc dust and alkali is red; the dyed black is fast to light and scouring agents.

Melanogen blue B, BG, D. When 1 : 5-dinitronaphthalene, dissolved in warm concentrated sulphuric acid, is treated with hydrogen sulphide or a metallic sulphide, a compound is produced which is precipitated as its insoluble zinc chloride compound from the diluted solution. This substance (1 kilo.), which is an intermediate product in the preparation of naphthazarin, is heated with sodium sulphide (5 kilos.) and sulphur (1 kilo.) at 150°–180° for several hours, when the fusion is poured into water and the filtered solution evaporated to dryness. This soluble colouring matter dyes cotton in fast greyish-blue shades which are not altered during dyeing by aerial oxidation, but subsequent treatment with copper sulphate develops a fast bluish-black shade. Subsequent treatment with chromium, nickel, or cobalt salts give bluish-blacks, whilst zinc, cadmium, or aluminium salts develop bright blue shades (*M.* D. R. PP. 114266, 114267, 116417, 119248, 120899, 124507). The non-sensitiveness of these dyes to aerial oxidation distinguishes them from the typical sulphide dyes which furnish oxidisable leuco derivatives.

Kryogen blue B, G, R, are similar dyestuffs produced by heating the reduction products of 1 : 5- and 1 : 8-dinitronaphthalene (*B.* D. R. PP. 88236, 92471, 92472) with sodium sulphide and sulphur; violet and blue shades are produced at 100°, whilst blacks are obtained at 150°–200°

(*B.* D. R. PP. 103987; *M. ibid.*, 128118). The intermediate naphthazarin product



is converted into a wool dye by alkali thiosulphate and then by the action of sulphites or bisulphites into soluble compounds, which dye chrome mordanted cotton in greenish-black shades (*B.* D. R. P. 147945).

Fast black B and BS. The former of these colouring matters consists of a mixture of two dyes produced by boiling 1 : 8-dinitronaphthalene with 3-5 molecules of aqueous sodium sulphide (1 : 120), then acidifying and boiling for 2 hours longer.

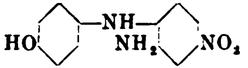
Fast black BS is produced by heating at 93° for 1 hour 200 parts of **fast black B** (30 p.c. paste) with 98 parts of sodium hydroxide (30°Be.) or the equivalent amount of sodium sulphide. The soluble product gives intense black shades on cotton (*B.* D. R. PP. 84989, 88847; Eng. Pat. 10996, 1893; 22603, 1894).

Anthraquinone black. 1 : 4′-Dinitro-anthraquinone (50 parts), sodium sulphide (250 parts), and sulphur (75 parts) are heated together until the product is soluble in water to a bluish-green solution.

Cotton is dyed with aqueous sodium sulphide in intense black shades. The colour is slightly soluble in alcohol to a green solution; with concentrated sulphuric acid the colour is greyish-black (*B.* D. R. PP. 91508, 95484; Eng. Pat. 15242, 1895).

Sulphide Blues.

Pyrogen direct blue (*Bl.*), the first blue sulphide dye discovered, is prepared from 2 : 4-dinitro-4′-hydroxydiphenylamine (m.p. 187°–188°) or its reduction product (m.p. 196°–197°)



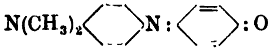
Ten parts of either of these substances are heated with 18 parts of anhydrous sodium tetrasulphide and 60 parts of alcohol in an iron or enamelled autoclave at 135°–145°. The reaction proceeds smoothly in alcoholic solution, colour formation begins at 110°, and after 3–4 hours the pressure reaches 8–10 atmospheres. Cotton is dyed in dark violet-blue shades with 2 p.c., and in black bluish-violet shades with 5 p.c. of the dye (Eng. Pat. 5385, 1900; D. R. P. 132424). The violet tint of the dye is increased by suspending it in water and adding hydrogen peroxide; ozonised air or steam produces a similar effect which is probably due to elimination of NH_2 groups. The violet product is fast to chlorine, light and scouring agents (D. R. P. 137784). When the temperature of the autoclave in the foregoing process is raised to 160°–170° **pyrogen grey** is produced, the shade of which is not affected by oxidising agents.

Pyrogen indigo (*Bl.*). Phenyl-4-amino-4′-hydroxydiphenylamine

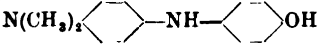
$$C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}OH$$

(27·6 kilos.), is heated with dry sodium pentasulphide (55 parts) in 150 litres of alcohol under reflux for 24 hours. The solvent is distilled off, the residue dissolved in water, and the dye precipitated by air as a dark blue powder, dissolving in aqueous sodium sulphide to a blue solution and dyeing cotton in indigo blue shades (D. R. P. 150553).

Immedial pure blue (*Immedial sky blue*) (*C.*). Nitrosodimethylaniline is reduced with iron powder in dilute acetic acid solution. After removing the iron the filtrate is mixed with the calculated amount of phenol in aqueous solution, and the mixture oxidised with air in the presence of copper salts. The resulting indophenol



is then reduced to 4-dimethylamino-4′-hydroxydiphenylamine



(m.p. 161°–162°) a base which is also obtained by heating *as*-dimethyl-*p*-phenylenediamine with *p*-aminophenol hydrochloride at 150°.

Twenty-five kilos. of this base are added gradually to 50 kilos. of crystallised sodium sulphide, 12·5 kilos. of sulphur, and 10 litres of water heated to 90°. The mixture is then heated under a reflux apparatus at 110°–115°, a green pitch separates and gradually redissolves. After 24 hours the product is dissolved in 500 litres of water, and the colour precipitated with 50 kilos. of salt. Cotton is dyed in shades resembling methylene blue which are superior to indigo blue in brilliancy of tint and in fastness to light, chlorine, acids, and milling (Eng. Pat. 16247, 1900; D. R. PP. 134947, 141752; Fr. Pats. 303524, 308669).

The *Bisulphite compound*

$$C_{14}H_{12}O_4N_2S_3,NaHSO_3,2H_2O$$

is the first crystallisable derivative obtained from sulphide dyes, and is used in purifying the foregoing colouring matter. The melt is dissolved in 700 litres of water and treated with sodium hydrogen sulphite until the additive compound is precipitated. The solution is then heated to 90°, when this substance dissolves, leaving the impurities. The bisulphite compound separates on cooling in yellowish needles, and is washed with brine solution; it dyes wool in acid baths, and with the aid of oxidising agents (chromates, copper salts, &c.) gives indigo blue shades. The colouring matter is regenerated by digesting the additive compound with dilute sodium hydroxide solution. The lower homologues of immedial pure blue have been described (D. R. P. Anm. K. 13405, 1900; D. R. P. 133481).

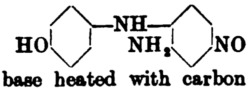
Eclipse blue (*G.*). The indophenol from dimethyl-*p*-phenylenediamine and phenol when treated with alkali sulphites gives a sulphonic acid with its sulphur in the nucleus containing the tertiary amino groups

$$N(CH_3)_2C_6H_3(SO_3H)NH{\cdot}C_6H_4{\cdot}OH.$$

The sodium salt of this acid heated at 120°–140° with an equal weight of sulphur and 2½ parts of crystallised sodium sulphide, gives a blue solution from which the colouring matter is precipitated by air, hydrogen peroxide, or alkali hypochlorite; cotton is dyed in very fast pure blue shades (Eng. Pat. 12578, 1901; D. R. P. 129325).

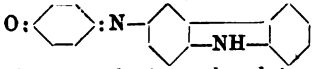
Immedial indone (*C.* D. R. P. 199963; Eng. Pat. 58, 1902; Fr. Pat. 317219; U.S. Pat. 709151). The indophenol from *p*-aminophenol and *o*-toluidine is heated with sodium polysulphide in alcoholic or aqueous solution (120°). The blue dye has a remarkable affinity for the cotton fibre, being much superior in this respect to its lower homologue from phenol and aniline. A brighter blue of redder shade has been obtained by heating the foregoing indophenol with sulphur alone at 190°–200° for 2 hours in the presence of hydrated chromic oxide. The product is directly applicable in sulphide solution as a cotton dye (*K. S.* Eng. Pat. 12879, 1903).

Thion blue B (*K.*). 2 : 4-Dinitro-4′-hydroxydiphenylamine, the condensation product of chloro-2 : 4-dinitrobenzene and *p*-aminophenol, is partially reduced to 4-nitro-2-amino-4′-hydroxydiphenylamine



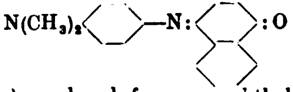
and this base heated with carbon disulphide, whereby the thiocarbamide derivative is produced. Five parts of this compound are heated for 10 hours at 145° with sodium sulphide (40 parts) and sulphur (24 parts). The fusion product is dissolved in water and the dye precipitated by the continued passage of air in the presence of sodium chloride. The shade on cotton is bluish-green, changed to pure blue by hydrogen peroxide, subsequent treatment with stannic chloride increasing the fastness of the dye (Eng. Pat. 19332, 1901; D. R. P. 139099).

Hydron blue. The indophenol

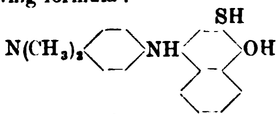


from carbazole and nitrosophenol is warmed with sodium sulphide (1·5 parts) until the colour disappears and then heated with sulphur (1–1·5 parts); the dye gives intense dark blue shades which are remarkably fast to light and chlorine (*C.* D. R. P. 218371).

Thiophor indigo (*C. J.*). The indophenol



(25 parts) produced from *a*-naphthol and *p*-aminodimethylaniline is heated in a reflux apparatus at 115° with 40 parts of crystallised sodium sulphide and 15 parts of sulphur. The leuco-indophenol which separates as an oil slowly reacts with the thionating mixture during 8–10 hours with evolution of hydrogen sulphide. The colouring matter, which crystallises from benzene in small prisms with a coppery lustre, still possesses the indophenol character of being hydrolysed by acids. On this account the leuco derivative of the dye is represented by the following formula :—



The solution of the dye in aqueous sodium sulphide is pale greenish-yellow, and, unlike the great majority of sulphide colouring matters, this product is soluble in the organic media, including ether.

Various shades of blue and violet are produced by changing the base employed in producing the indophenol; *p*-phenylenediamine and 2 : 4-tolylenediamine give rise to dark violet tints. The temperature is generally kept below 160°, and alterations in tinctorial properties are effected by introducing alcohol or glycerol into the thionating mixture. The dyed colours are fast to light, alkalis and scouring agents, but are destroyed by acids (D. R. P. 179839; Eng. Pat. 17540, 1905; Fr. Pat. 357587; U.S. Pat. 821378).

A series of sulphide blues having the property of dyeing weak blue shades from sodium sulphide baths, and remarkably fast blue shades when employed as vat dyes, are produced by heating with sodium polysulphide (Na_2S_5—Na_2S_8) in alcoholic solution, the indophenols from dialkyl-*p*-phenylenediamines and phenol and its ortho- and diortho-chloro derivatives (*B.* D. R. PP. Anmeldung, 60985 and 62302, 1911). Similar sulphide blues capable of employment as vat dyes are obtained in a similar manner from the indophenolthiosulphonic acids (prepared from alkyl-*p*-diaminethiosulphonic acids and phenol), or from the corresponding thiazines (*B.* D. R. PP. 153361; Anmeldung, *B.* 60984, 1911).

Other commercial brands of sulphide blues :— **Immedial direct blue, B, JB, R, OD; Immedial indogene B, GCl; Thiogene blue, B, R, 2R; Thiogene cyanine B, O, G; Thiogene deep blue RL, 2RL; Thiogene new blue JL, Bl, 2RL; Thionol blue 2B, RB, 2RF.**

SULPHIDE GREENS.

Italian green, *Verde Italiano* (Lepetit, Dollfus, and Gansser, D. R. P. 101577). *p*-Nitrophenol (12·5 kilos.), copper sulphate (4·5 kilos.) in 30 litres of water, are mixed with sodium hydroxide (19 kilos.), sulphur (17·5 kilos.), in 17 litres of hot water, and the mixture gradually heated to 210°, ammonia being evolved. Cotton is dyed in dull grass-green shades which appear pure green by artificial light. Hydrogen peroxide, chromic acid, or copper sulphate change the colour to blue-black, and concentrated oxidising agents discharge the colour, this reaction being made use of in printing with the dye.

Pyrogen green B, FB, FF, 2G, 3G, (*Bl.* D. R. P. 148024), **pyrogen dark green B.** *p*-Aminophenol (8 parts), sodium sulphide (50 parts), sulphur (20 parts), copper bronze (1 part), and water (100 parts) are heated to 170° in 3 hours. Cotton is dyed in olive-green shades; copper is present in the ash of the dyed fibre.

The greater the amount of copper bronze the more olive is the shade of colour produced. Other variations in the tint are brought about by using the homologues and substitution products of *p*-aminophenol.

Pyrogen olive N (*G.* D. R. P. 135335). *p*-Hydroxybenzylidine-*p*-nitroaniline, *p*-nitrobenzylidene-*p*-aminophenol and similar methylene and benzylidene derivatives of *m*- and *p*-diamines, and aminophenols are heated to 180°–200° with sodium polysulphide with or without metallic salts.

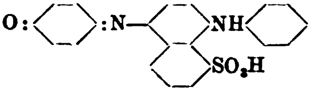
Eclipse green G (*G.* D. R. P. 135410; Eng. Pat. 26448, 1901). The indophenol from *p*-aminodimethylaniline and phenol is treated with sodium sulphite, and the resulting sulphonic acid (40 parts, Na salt) heated with sodium sulphide (100 parts), sulphur (40 parts), and copper sulphate (10 parts) in a reflux apparatus at 125°–130°. The dye is precipitated by air from its solution in aqueous sodium sulphide; it dyes in yellowish-green shades fast to light and soap.

Thion green B (*K.* D. R. P. 138104; Eng. Pats. 9619, 16931, 1902; Fr. Pats. 320701, 323489). Hydroxyphenylthiocarbamide and hydroxythiocarbanilide are heated respectively with sodium polysulphide at 140°–180°, the former gives a blue-green and the latter a mignonette-green, both dyes are turned bluer by chromic acid, and are insoluble in strong sulphuric acid. The dye is purified by dissolving the fused mass in water, acidifying slightly, filtering off the precipitated sulphur, and salting out the colour in the filtrate.

Immedial green. 4-Dimethylamino-4′-hydroxydiphenylamine (50 kilos.) is added to a solution of sulphur (31 kilos.) in crystallised sodium sulphide (124 kilos.). When the base has dissolved, copper sulphate (10 kilos.) is added, and the temperature raised to 120° and maintained for 24 hours. The dye is precipitated by salt or calcium chloride from the resulting solution; it dissolves in strong sulphuric acid to a green solution, and in aqueous sodium sulphide or hydroxide to a reddish-violet solution. The bluish-green shade on cotton is very fast (*C.* D. R. P. 129540).

An olive-green (*O.* D. R. P. 146064) is obtained by heating diformyl-*m*-phenylenediamine with sodium polysulphide at 110°, and then with the further addition of zinc chloride at 230°.

The 1 : 8- derivatives of naphthalene are employed in producing sulphide greens. Phenyl-α-naphthylamine-8-sulphonic acid and *p*-aminophenol yield an indophenol



which gives a green on heating with sodium polysulphide in the presence of copper sulphate. The perimidines produced by condensing 1 : 8-naphthylenediamine with aldehydes, ketones, and aliphatic acids (Annalen, 1909, 365, 53; Ber. 1909, 42, 3674) yield indophenols with *p*-aminophenol, and its chloro derivatives (*e.g.* 2 : 6-dichloro-*p*-aminophenol). These indophenols, when heated for 60 hours in a reflux apparatus with alcoholic sodium polysulphide, give rise to very fast dark green colouring matters (*A.* D. R. P. Anmeldung, 20316. 1911).

Other commercial brands of sulphide greens :— **Immedial deep green G; Thionol green 3G; Thionol brilliant green GX, 3GX, 4GX; Thionol dark green; Thiogene green G, GG, GL; Thiogene olive green GG, GGN.**

Sulphide Browns.

Cachou de laval (*P.*) is usually prepared from sawdust and other waste products allied to cellulose by heating these materials with sodium polysulphide at 250°–300°, the higher the temperature the darker the shade of brown produced (*cf.* Richardson and Akroyd, J. Soc. Chem. Ind. 1896, 328).

In all probability the final products of this reaction are phenolic in character, inasmuch as cellulose yields phenol on distillation, and the latter on oxidation passes into phenoquinone, a substance containing three benzene nuclei, which on heating with alkali polysulphide under pressure gives a dye resembling cachou (Wichelhaus, Ber. 1872, 5, 248; 1907, 40, 126; 1910, 43, 2926). A similar brown sulphide dye is produced by heating crude cresol with sodium polysulphide at 170°–250° (*By.* D. R. P. 102897; Eng. Pat. 22417, 1895).

Cachou de laval S is the soluble product formed by digesting the precipitated colouring matter of cachou with alkali sulphites or bisulphites; it is used in printing (D. R. P. 88392).

Thiocatechin (*P.* D. R. P. 82748; Eng. Pat. 3414, 1895; Fr. Pat. 239714; U.S. Pat. 561276; Ber. 1880, 13, 1226). The acetyl derivatives of aromatic diamines and nitro-amines are heated either with sulphur alone or with sulphur and sodium sulphide at 200°–250° for 3 hours.

The dye dissolves in aqueous sodium sulphide to a yellowish-brown solution, and when dyed on cotton requires to be fixed by subsequent oxidation. Various shades of yellow and brownish-yellow are produced by heating with 2 parts of sulphur, the following aromatic substances: acetyl-*p*-phenylenediamine, aceto-α-naphthalide, acetyl-*p*-nitroaniline, diacetyl-di-*o*-nitrobenzidine, and the acetyl derivatives of nitro-, *o*-, and *p*-toluidine

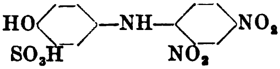
$[CH_3 : NH_2 : NO_2 = 1 : 2 : 4 \text{ and } 1 : 4 : 2]$

Thiocatechin S is the soluble product obtained by digesting thiocatechin with aqueous sulphites or bisulphites.

Cattu Italiano, sulphine brown (Lepetit, Dollfus, and Gansser, D. R. P. 118701; Eng. Pat. 18900, 1899; Fr. Pat. 290714). Turkey-red oil (5 parts), the higher fatty acids, and especially the unsaturated acids and their esters and alkali salts, when heated with sodium carbonate (12 parts) and sulphur (10 parts) at 320°–330°, evolve carbon dioxide, hydrogen sulphide, and volatile organic matter. The product is a black porous mass readily soluble in water. In spite of the different starting materials which are utilisable in this process, the colouring matter is very constant in properties; it dyes cotton brown from a bath containing sodium chloride in shades which are brighter than the cachous, but less fast to light and chlorine. The dye dissolves in water or aqueous sodium sulphide to solutions which are green to blue in colour, depending on the temperature at which the colouring matter was originally produced.

Thion brown (*K.* D. R. P. 137540; Eng. Pat. 18489, 1896; Fr. Pat. 315648; U.S. Pat. 723448). Chrysoidine base R (*H.*) (*v.* Azo-colouring matters), benzeneazotolylene-2 : 4-diamine (30 parts) are added to crystallised sodium sulphide (80 parts) and sulphur (30 parts) at 110°–120°, and the temperature raised to 160°, when the azo compound is decomposed with elimination of aniline. The viscid mixture is then baked for 1–2 hours at 160°–170°, and finally for 3–4 hours at 200°–220°, when a brownish-black powdery mass is produced which dyes cotton in intense yellowish-brown shades very fast to light. The dye is precipitated by acids from its alkaline solutions, dissolving as a dark brown mass in alcohol or concentrated sulphuric acid to brown solutions.

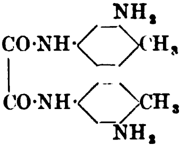
Sulphanil brown (*K.* D. R. P. 125584). 2 : 4-Dinitro-4′-aminodiphenylamine, prepared from chloro-2 : 4-dinitrobenzene and *p*-phenylenediamine is converted by means of aqueous alkali sulphite at 150° (46 p.c.) into the sulphonic acid.



This compound (40 parts), dissolved in twice its weight of water, is heated at 140°–160° with sodium sulphide (80 parts), sulphur (30 parts), and water (100 parts) until the mass is dry. The aqueous solution of the dye is violet-black changed to brown by caustic alkali.

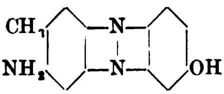
Cotton brown (*D.* D. R. PP. 102821, 106039). The higher nitrated derivatives of diphenylamine obtained by treating the base with concentrated sulphuric and nitric acids at 25°–60° yield a brown dye when cautiously reduced with sodium sulphide or polysulphide, and the reduction product dried at 200°. The colour is soluble in water, and dyes in cold or hot baths (*cf.* Eng. Pat. 18924, 1903).

Eclipse brown, N, R, B, G, 3G, V (*G.* D. R. PP. 125586, 125587, 126964, 128659; Eng. Pat. 1644, 1901; Fr. Pat. 306655). Tolylene-2 : 4-diamine (34 parts), oxalic acid (17 parts), sodium sulphide (120 parts), and sulphur (40 parts) are heated to 225°–250°, and then to 300°. The process may be varied by taking molecular proportions of the diamine and of tolylene-2-amino-4-oxamide



and the polysulphide may be replaced by a solution of sulphur in aqueous sodium hydroxide. The dye dissolves in water to a chestnut-brown solution, being precipitated therefrom by boiling with dilute mineral acid. Hydrogen sulphide is evolved on reducing the compound with zinc dust. In these condensations the oxalic acid may be replaced by succinic and phthalic acids, the latter giving rise to brown colouring matters dyeing very fast catechu shades.

A brown colouring matter of the immedial series, dyeing cotton in very fast shades closely resembling natural catechu, is produced by oxidising a mixture of *p*-aminophenol and tolylene-2 : 4-diamine to 2-methyl-3-amino-6-hydroxyphenazine



and by heating the azine obtained from 15·8 parts of *p*-aminophenol with 100 p.c. sodium sulphide (42 parts) and sulphur (80 parts) for 20 hours at 135° (*C.* D. R. P. 208109; Fr. Pat. 382412; *cf. By.* Eng. Pat. 19548, 1907; *B.* D. R. P. 147990). Similar fast catechu shades are produced by heating at 250° tolylene-2 : 4-diamine (2 parts), acetyltolylene-2 : 4-diamine (1 part), and sulphur (8 parts), the product being ground with 3 parts of sodium hydroxide and warmed at 130° (*A.* D. R. PP. 221493, 229154; Eng. Pat. 24703, 1909; Fr. Pat. 419665).

A mixture of methyleneresorcinol or its polymerides (Ber. 1892, 25, 947; 1894, 27, 2888), *p*-phenylenediamine, sodium sulphide, and sulphur when heated gradually to 200°–220° gives very fast yellowish catechu shades (*O.* D. R. P. 167429; Eng. Pat. 13950, 1905; Fr. Pat. 355783).

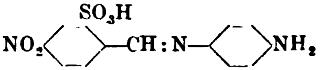
Immedial brown B, dark brown A (*C.* D. R. P. 112484; Eng. Pat. 25754, 1899; Fr. Pat. 295593). 4-Hydroxy-4′-aminodiphenylamine is boiled with aqueous sodium hydroxide and the product heated to 160° with sodium polysulphide. The two changes may be effected in one operation. This colouring matter gives on cotton intense yellow-brown shades, rendered yellower and faster by after-chroming.

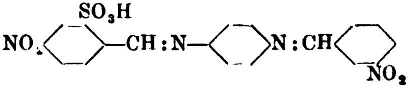
Among other sulphide browns of similar origin to the foregoing colouring matters may be mentioned the following:—

Katigen brown (*By.*); **Sulphur brown G** (*A.*); **Sulphur cutch** (*A.*); **Kryogen brown** (*B.*); produced from 1:8-dinitronaphthalene; **Immedial cutch, immedial khaki, immedial catechu** O.G. and O.R. (*C.*).

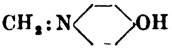
SULPHIDE YELLOWS.

Pyrogene yellow M, O, OR, 3R (*Bl.* D. R. P. 135335; Eng. Pat. 1007, 1900; Fr. Pat. 295712). These colouring matters were the first sulphide yellows discovered, and are produced by heating with sodium sulphide and sulphur (either with or without metallic salts), various condensation products of aromatic *p*-diamines, and amino- and diamino-phenols with formaldehyde, benzaldehyde, the nitrobenzaldehydes, and nitrobenzyl chlorides. The compounds with these aldehydes are of the nature of anhydro bases (Schiff bases). The two following derivatives, which may be regarded as typical of the members of the series, give respectively in the polysulphide fusion colours dyeing in greenish-yellow (I.) and orange-yellow (II.) shades.


I.


II.

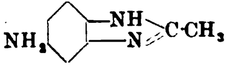
Other derivatives give rise to different shades, methylene-*p*-aminophenol



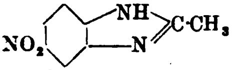
gives a brown, whereas *p*-nitrobenzylidene-*p*-aminophenol

furnishes an olive dye.

Kryogen yellow R (*B.* D. R. P. 142155). 2 : 4-Dinitroacetanilide when reduced with iron filings and dilute acetic acid yields the anhydro-base, 5-amino-2-methylbenziminazole



This base is heated at 200°–230° for 2–3 hours with 2 parts of sulphur, the product ground with an equal weight of sodium sulphide, dissolved in water, the mixture dried and baked at 200°–230° for 1–2 hours. This colouring matter is diazotisable on the cotton fibre. A similar dye giving greener shades is produced by heating the nitro-anhydro base



with sulphur and an equal weight of benzidine at 200°–240° until hydrogen sulphide is no longer evolved (*TM.* D. R. P. 157862; Eng. Pat. 5449, 1905; *cf.* *A.* D. R. PP.121463, 146916, 147403, 147729, 150915, 152717, 154108).

Immedial yellow D (*C.* D. R. PP. 139430, 141576; Eng. Pat. 11771, 1902; Fr. Pat. 321122). Tolylene-2:4-diamine (50 kilos.) and sulphur (100 kilos.) are heated gradually during 2 hours up to 190°. The amorphous sulphur compound produced is brownish or orange-yellow, insoluble in all ordinary media, dilute acids, or aqueous alkalis, but dissolving slightly in concentrated sulphuric acid to a brown solution. This substance (100 kilos.) is powdered and gradually added to crystallised sodium sulphide (90 kilos.) in water (60 kilos.) at 110°.

The mixture is heated at 120° until the organic compound becomes soluble. The solution is diluted, acidified with hydrochloric acid, and the yellow precipitate collected. The final product, which is soluble in aqueous alkali hydroxides or sulphides, gives on cotton yellow shades which are fast to scouring agents and acids; it is almost insoluble in concentrated sulphuric acid.

Thion yellow G, GG, GN (*K.* D. R. P. 139429; D. R. P. Anm. K. 24649; Eng. Pat. 16932, 1902; Fr. Pat. 323490). Tolylene-2:4-diamine and sulphur interact, forming a thio derivative (m.p. 145°), which when dissolved in hot aqueous sodium sulphide furnishes a yellow colouring matter precipitated by carbon dioxide from the alkaline solution.

The aromatic *m*-diamines yield complex thiocarbamides when heated with carbon disulphide (Ber. 1885, 18, 3293), and these thio derivatives when heated with sulphur at 150°–170° give rise to similar yellow dyes which are dissolved in aqueous sodium sulphide. Benzidine is sometimes added during fusion (*M.* D. R. PP. 152027, 153916, 166864; *A.* *ibid.* 171871). Tolylene-2:4-diamine itself yields a yellow dye when fused with benzidine and sulphur at 190°–280°, the product being rendered soluble by sodium sulphide (*M.* D. R. P. 163143; *TM.* D. R. P. 163001).

Immedial orange C, N (*C.* D. R. P. 152595; Eng. Pat. 11898, 1902; Fr. Pat. 321183). Tolylene-2:4-diamine (50 kilos.) and sulphur (125 kilos.) are heated in an iron pan with stirrers until hydrogen sulphide is no longer evolved, and the product baked at 250° until a hard brittle mass is produced, which is then added to sodium sulphide (150 kilos.) at 110°–120°. The mixture is dissolved in water, and the colouring matter precipitated by acid. Cotton is dyed in orange-brown shades which are brightened by hydrogen peroxide, but scarcely affected by chromic acid. This colouring matter is insoluble in concentrated sulphuric acid.

Eclipse yellow G, 3G (*G.* D. R. PP. 138839, 145762, 145763). When heated with commercial formic acid in a reflux apparatus, tolylene-2:4-diamine gives rise to formyltolylene-2:4-diamine, very sparingly soluble pyramids, m.p. 113°–114°, and diformyltolylene-2:4-diamine, acicular aggregates, m.p. 176°–177°. These products, which are separated by fractional crystallisation from water, the latter being the more soluble, are both used in the preparation of sulphide dyes. The formyl derivative is added to a solution of an equal weight of sulphur in 3 parts by weight of crystallised sodium sulphide fused in its water of crystallisation and the temperature raised to 240°. The dye, which is obtained as a light brown precipitate on acidifying a solution of the fusion, gives bright yellowish-orange shades, those from the monoformyl derivative having the browner tint. The thionation may also be effected by sulphur, either alone or with the addition of benzidine or other analogous bases. The formyl derivatives may be replaced by the condensation products of tolylene-2:4-diamine and oxalic acid (*M.* D. R. PP. 156177, 157103).

Similar sulphide yellows are produced by fusing with sulphur at 200°–220° mixtures of tolylene-2:4-diamine and its diformyl derivative or diformylbenzidine (*G.* D. R. PP. 146917; *A.* 159097, 170746), and various shades of yellow, yellowish-brown, and orange are obtained by employing mixtures of tolylene-2:4-diamine and various aromatic nitro derivatives, such as the nitranilines and their homologues, and the dinitro-benzenes and -naphthalenes (*By.* D. R. PP. 201834, 201835, 102836).

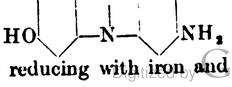
Immedial yellow GG (*C.* D. R. P. 180162; Eng. Pat. 4097, 1906; Fr. Pat. 372137; U.S. Pat. 892455). The relationship between sulphide yellows and thiazole dyes is illustrated by the employment of dehydrothiotoluidine (*v.* PRIMULINE) in the sulphur fusion. Benzidine (19 parts), dehydrothiotoluidine (16 parts), and sulphur (70 parts) are heated together for 1 hour at 210°, and the fusion digested with fused sodium sulphide at 120° until rendered soluble. The dye is then precipitated by mineral acid. Cotton is dyed in greenish-yellow shades very fast to scouring agents (*cf.* *B.* Rassow, D. R. P. 234638).

Among the numerous other yellow sulphide dyes are **Thioxine yellow** and **Thioxine orange,** yellowish powders slightly soluble in concentrated sulphuric acid and insoluble in sodium hydroxide; **Thionol yellow G, R; Thionol orange; Thiogene yellow G, GG, 5G.**

REDDISH SULPHIDE DYES.

Although bright red sulphide dyes have not yet been obtained, it has been found possible to produce various shades of purple, violet, and maroon by thionating certain red colouring matters. In these reactions sulphur is probably introduced into the molecule without destroying the complex to the presence of which the red colour is due.

Immedial maroon, bordeaux, and violet (*C.* D. R. P. 126175; Eng. Pat. 14836, 1900; Fr. Pat. 303107; U.S. Pat. 701435). The simplest starting material for the production of the bordeaux-red sulphide dyes is 6-amino-3-hydroxyphenazine



prepared by reducing with iron and acetic acid

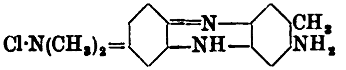
2 : 4-dinitro-4′-hydroxydiphenylamine (from *p*-aminophenol and chloro-2 : 4-dinitrobenzene) and oxidising the resulting hydroxytriamine

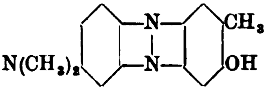
$$HO{\cdot}C_6H_3(NH_2)NH{\cdot}C_6H_4{\cdot}NH_2$$

in alkaline solution with manganese dioxide.

The sulphonic and carboxylic acids of this phenazine, which are obtained in a similar manner, are also employed in the sulphide fusion.

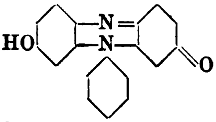
Tolylene red (neutral red), 6-dimethylamino-3-amino-2-methylphenazine obtained by oxidising a mixture of dimethyl-*p*-phenylenediamine and tolylene-2 : 4-diamine, is too insoluble for employment in the sulphide fusion, and is converted either into its sulphonic acid by fuming sulphuric acid (23 p.c. SO_3) or into the corresponding hydroxy-azine by hydrolysis with water under pressure.





These products being soluble in aqueous alkali hydroxides or sulphides are utilisable in the production of reddish sulphide dyes.

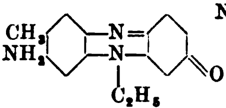
Safranol, 3-hydroxy-6-oxy-N-phenylphenazine produced either by condensing nitrosophenol with *m*-hydroxydiphenylamine, by oxidising this base mixed with *p*-aminophenol or by the alkaline hydrolysis of phenosafranine or phenosafraninone, is employed in the sulphide fusion, as is also phenosafranine and its carboxylic and sulphonic acids.



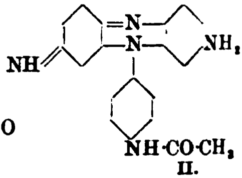
One of the foregoing azines (10 parts) is added to a solution of sulphur (20 parts) in sodium sulphide (50 parts) and water (10 parts), and the mixture heated to 140°–150° until the product dissolves in water to a dark violet solution. This operation may also be carried out either in a reflux apparatus or in an autoclave. The sulphide dyes from 6-amino-3-hydroxyphenazine and its carboxylic and sulphonic acids, and from the alkali soluble tolylene red derivatives give brownish-violet shades, the safranol condensation product dyes in bluish-violet tints, whereas reddish-violet shades are obtained from the dyes derived from N-ethylsafranol and from phenosafraninone and its carboxylic and sulphonic acids.

The fusion of these phenazine derivatives is also carried out in the presence of metallic salts ($CuSO_4$, $CoSO_4$, or $NiSO_4$, *cf. Lev.* Eng. Pats. 24008, 1906; 17749, 1907), the resulting dyes being redder and faster than those produced in the absence of these adjuvants.

3-Amino-6-hydroxyphenazine and its C-methyl homologue when heated to 120°–140° with aqueous sodium polysulphide and copper sulphate or metallic copper give dark red sulphide dyes. Safranol and safraninone when similarly treated yield violet-red colours and N-ethyl-2-methylsafraninone (I.) gives rise to a bordeaux-red dye. *p*-Acetylaminosafranine (II.) (N-acetylaminophenyl-3 : 6-diaminophenazine) and its homologues when heated at 120° for 20 hours with aqueous sodium polysulphide containing copper sulphate give rise to bluish-violet dyes precipitated by acid, which are faster and brighter than those prepared from the simpler safranines (*M.* D. R. PP. 171177, 177709, 179021, 222418; Fr. Pat. 361608; U.S. Pat. 818980).



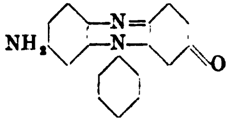
I.



II.

Azines without hydroxyl groups, such as tolylene red, being insoluble in alkali sulphides, are first fused with sulphur at 180°–230°, the product being then treated with sodium sulphide at 180°. Cotton is dyed in reddish-brown shades (*B.* D. R. P. 147990).

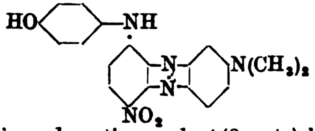
Thiogen purple (*M.* D. R. P. 181125; Eng. Pat. 2797, 1906; Fr. Pat. 372277; U. S. Pat. 829740). The N-alkylated aminohydroxyphenylphenazines and their tolyl homologues, the chloro derivatives of the azines (produced from chloroaminophenols) when heated at 110°–135° in a reflux apparatus or under pressure with aqueous or alcoholic sodium polysulphide give sulphide colouring matters dyeing cotton in clear bordeaux-red shades, the higher the temperature of the fusion the bluer the tint produced. Reddish-violet and dark red sulphide dyes are obtained by heating in a reflux apparatus at 110°, the chloro- and bromo-phenazines and the corresponding halogenated toluazines with aqueous sodium polysulphide in the presence of copper sulphate (*M.* D. R. P. 174331; *A. ibid.* 207096). In these condensations the halogen radicle of the chloro- or bromo- azine is readily replaced by a SH group, and accordingly the organic base is first heated with sodium sulphide alone at 110°–140°, and subsequently treated with polysulphide at a high temperature. When the latter operation is omitted intermediate mercaptan derivatives of the hydroxyphenazines are produced which have only a slight affinity for the cotton fibre and are converted into sulphur dyes by fusion with alkali polysulphide (*M.* D. R. PP. 181327, 187868; Fr. Pat. 360437).



Thiogen violet V, B (*M.* D. R. PP. 168516, 177493, 179960, 179961). Phenosafraninone, 3-oxy-6-amino-N-phenylphenazine (10 parts) warmed at 115°–120° with sulphur (30 parts), alone or with a diluent, then heated further to 200°, and mixed with sodium sulphide. The violet dye produced, which contains sulphur, is converted into a colouring matter, dyeing bluer and faster shades by heating for 20 hours in a reflux apparatus at 135° with twice its weight of aqueous sodium polysulphide. The addition of copper sulphate or copper to the foregoing polysulphide fusion leads to the production of redder and faster shades of violet, the redness increasing with the amount of copper employed in the condensation.

Violet to violet-blue shades of sulphide dyes are produced by heating at 170° for 3 hours safranol (10 parts), sulphur (30 parts), and aniline (10 parts), or some other organic solvent of high boiling-point (*e.g.* dimethylaniline, benzidine). Bluer and more sombre tints are obtained either by prolonging the heating or by raising the temperature to 240° (*M.* D. R. P. 178982; Fr. Pat. 360437).

Thion violets (*K.* D. R. PP. 144157, 152373, 160790, 160816, 165007). 4-Nitro-2-amino-4′-hydroxydiphenylamine and nitrosodimethylaniline hydrochloride condense to form the complex azine 1-nitro-4′-*p*-hydroxyphenylamino-6-dimethylaminophenazine.



This condensation product (8 parts), heated at 130°–140° for 2–3 hours with sodium sulphide (40 parts) and sulphur (16 parts), yields a violet sulphide dye dissolving in water to a dark green solution, and in concentrated sulphuric acid with a bluish-green coloration.

Trihydroxyphenylrosinduline is obtained by the condensation of *p*-aminophenol and benzene-azo-*a*-naphthylamine hydrochloride, or from the former compound and *a*-nitronaphthalene (*K.* D. R. PP. 158077, 158100, 158101, 160789 160815, 163239). This rosinduline (52 parts), heated for 5 hours at 160°–170° with sodium sulphide (160 parts), sulphur (40–60 parts), sodium hydroxide (40°Be, 24 parts), and water (200 parts), gives rise to a reddish-violet dye dissolving in concentrated sulphuric acid to a blue solution.

The indophenol from *p*-aminophenol and *p*-xylenol when heated with aqueous sodium polysulphide in a reflux apparatus for 16 hours or under pressure (125° for 12 hours), or in alcoholic solution for 2–3 days, gives rise to a sulphide violet which separates from solution in small brown crystals having a metallic lustre. This colouring matter dissolves in aqueous sodium sulphide to a blue solution, and dyes in deep violet shades which are very fast and, hitherto, unsurpassed in intensity (*C.* D. R. PP. 191863; Eng. Pat. 4653, 1902; Fr. Pat. 318577).

MANUFACTURE OF SULPHIDE DYES.

The apparatus most generally employed in the polysulphide fusion is a cylindrical cast-iron jacketed pan about 3 ft. deep by 2 ft. in diameter, and having a capacity of about 100 gallons. The jacket serves for the introduction of superheated steam, a pressure of 4–6 atmospheres sufficing to raise the temperature of the fusion to 125°–135°. The pan is fitted with a mechanical stirrer and its domed lid contains a man-hole for introducing the reagents, a thermometer tube dipping into the fusion, an opening leading to the reflux condenser, and an inlet tube for air under increased or decreased pressure. The jacket is fitted with a manometer, and if the pan is to be used for fusions under pressure, it is also fitted with a pressure gauge. This plant serves for the majority of modern sulphide fusions (*e.g.* dinitrophenol black), which are carried out at temperatures only slightly above the boiling-point of water (105°–120°). In fusions requiring higher temperatures (*e.g.* 200°–300°, cachou de laval, eclipse brown, &c.) smaller cast-iron pans are employed, heated either by direct fire or in an oil bath, the fittings of the melting-pan being similar to those of the jacketed pan. Vaseline or a high-boiling liquid (*e.g.* aniline, b.p. 182°) may be employed in the oil bath, which is preferable to heating by direct fire, as local overheating is avoided. This mode of heating is employed both in sulphide melts and in fusions with sulphur alone in the production of yellow.

Sulphur fusion. This fusion is restricted chiefly to the production of sulphide yellows, oranges, and browns, which, being allied to the thiazole dyes (*v.* PRIMULINE), are prepared in a similar way. A few bases give blue and black sulphide dyes with sulphur alone at comparatively low temperatures, 2 : 4-diaminophenol, for instance, with sulphur at 80°–120°, gives a colour dissolving in sodium sulphide to a blue solution, and dyeing cotton in bronzy black shades, which, however, are not fast to chroming (Vidal, Eng. Pat. 16449, 1896). The products of the sulphur fusion for yellows are insoluble substances, which are ground up and rendered soluble by boiling with concentrated aqueous sodium sulphide.

Sulphide fusion. The heating of nitro compounds and sulphur is avoided, so far as possible, owing to the risk of explosion, and in general the sulphide fusion is carried out with a mixture of sodium sulphide and sulphur (sodium polysulphide Na_2S_2 . . . Na_2S_5) generally in the presence of water either added or derived from the commercial crystallised sulphide $Na_2S,9H_2O$.

In the case of nitro compounds yielding easily decomposable polyamines on reduction, it is preferable to add the organic substance to the fused polysulphide rather than to reduce the nitro compound with sodium monosulphide before introducing the sulphur.

In the Vidal black process the *p*-aminophenol produced by reduction from *p*-nitrophenol is comparatively stable, and consequently the sulphur can be added after reduction. With dinitrophenol, however, the best result is obtained by adding the nitro compound to the polysulphide in aqueous solution when reduction and thionation occur concurrently. The black obtained by reducing dinitrophenol with aqueous monosulphide, and then adding sulphur, is distinctly inferior in tinctorial properties to Cross dye black BX (*H.*).

At high temperatures sodium monosulphide will act as a thionating agent, for, on reducing nitro compounds, it becomes itself converted into a complex mixture of sulphites, polysulphides, and thiosulphates. A sulphide brown is produced by fusing dinitrophenol at 160°–180° for 6–8 hours with crystallised sodium sulphide.

The fusion under reflux condenser, which is employed when the formation of colour occurs at temperatures near 100°, is of great utility in the manufacture of blacks from dinitrophenol, picric, and picramic acids, 2 : 4-dinitro-4′-hydroxydiphenylamine and its chloro derivatives and especially in the production of blues from indophenols, and of violets from hydroxy and amino derivatives of the azines.

Alcoholic condensation. The thionation is often carried out in alcoholic solution, the sulphide employed being either anhydrous or crystalline. In this medium sulphur dissolves readily to an extent corresponding with the tetrasulphide Na_2S_4. Although on account of the low temperature (80°) the condensation takes a long time, yet the products are obtained in a very pure condition, the dyes derived from certain indophenols separating in a crystalline form. The alcoholic or aqueous fusions are sometimes effected under pressure. Immedial black, when prepared in this way from 2 : 4-dinitro-4′-hydroxydiphenylamine or its reduction products, separates as a crystalline dark blue lustrous powder dyeing in very intense black shades.

Additions to the sulphide fusion. Sometimes the temperature of the condensation is raised either by substituting amyl alcohol for water or ethyl alcohol, or by adding to the fusion such inert substances as glycerol, naphthalene, or β-naphthol. Aromatic amines have also been added to sulphide fusions, but in some cases they take part in the condensation. Benzidine, for example, is frequently added to sulphur fusions for yellow. Dehydrothiotoluidine, when melted with sulphur alone, gives no colouring matter, but when benzidine is introduced into the melted mixture immedial yellow GG is produced (*C.* D. R. P. 180162).

Copper is added to many sulphide fusions, most frequently in the form of sulphate, but also as copper bronze; it imparts greenish shades to black, reddish shades to browns and violets and yellowish shades to red. In some cases this metal alters the chemical properties of the dye without greatly modifying its shade of colour. The immedial black fusion in presence of copper gives a greenish instead of a bluish-black, which, unlike ordinary immedial black, is not oxidised on the fibre by hydrogen peroxide to immedial blue. It is often immaterial whether the copper is added during thionation or afterwards. Zinc salts are added to fusions of 1 : 8-naphthalene derivatives to prevent the formation of brown impurities during the preparation of certain blue sulphide dyes (*By.* D. R. P. 116655).

The condensation of the indophenol

$$p\text{-}NH_2\cdot C_6H_4\cdot N : C_6H_4 : O$$

with aqueous polysulphide does not give a satisfactory colour unless manganous sulphate is added to the fusion when an indigo blue dye is produced (*P.* D. R. P. 22406; Fr. Pat. 406225).

The course of the sulphur and polysulphide fusions may be ascertained by dissolving samples in water or sodium sulphide, and precipitating the sulphide dye and excess of sulphur with dilute acid. The acid filtrate contains the unthionated amines which may be recognised in one of three ways: (1) By diazotisation and coupling with alkaline β-naphthol; (2) oxidation to indophenols; (3) production of coloured solutions: this occurs in the case of the azines and other coloured bases. The fusion product is dissolved in water, or if necessary, aqueous sodium sulphide, and in some cases (*e.g.* dinitrophenol black) the colour is precipitated from the filtered solution of its leuco derivative by passing in a current of air. This precipitation by air sometimes takes place, however, with considerable difficulty, and then the colouring matter is precipitated by dilute acid in a wooden vat surmounted with an efficient draught hood for carrying off the torrent of hydrogen sulphide set free when the alkali sulphide solution is acidified. In other cases the dye is salted out with sodium, ammonium, or calcium chloride, or other soluble salts. The precipitated dye is collected either in a filter press or on a vacuum filter, the latter being employed only when the precipitate is not too slimy.

Immedial pure blue is purified either through the soluble bisulphite compound or by dissolving the leuco derivative of the colouring matter in hydrochloric acid, filtering from insoluble impurities and precipitating the hydrochloride of leuco immedial pure blue by the addition of brine solution.

The Dyeing of Sulphide Colours.

The sulphide dyes are best dissolved in wooden vessels by pouring over them boiling water containing sufficient sodium sulphide to bring the colours into solution. Copper or brass vessels are to be avoided, and the metallic parts of the dyeing apparatus should consist of iron or lead. The dyeing operation is carried out in wooden or iron vats heated by steam coils. In addition to sodium sulphide, the bath is generally prepared with sodium carbonate and either sodium chloride or sulphate. In the following dyeing recipes the percentage of ingredients is always reckoned on the weight of dry cotton, which is generally dyed in about 20 times its weight of water.

Sulphide blacks. For dyeing 100 grms. of cotton yarn in a full shade of cross dye black BX (*H.*), 10 grms. of this colour are dissolved in 500 c.c. of hot water containing 20 grms. of crystallised sodium sulphide and 5 grms. of sodium carbonate. This mixture is boiled for 5 mins., the solution made up to 2 litres, the yarn, which has been previously well boiled out with water, is then introduced, and the bath kept boiling for 15 mins. This temperature is maintained for 30 mins. longer, during which period 75 grms. of salt are gradually added, the bath being kept up to constant volume by the addition from time to time of hot water. The dyed yarn is then lifted and rinsed in cold water.

Although after-chroming does not materially alter the shade of black which is fully developed as the result of aerial oxidation, nevertheless this treatment is sometimes used to increase the fastness of the dye, and is effected by immersing the rinsed yarn for 30 mins. at 60° in 2 litres of water containing 2 p.c. of sodium or potassium bichromate, and 2 p.c. of sulphuric acid. Any bronziness due to oxidation or excess of colour is removed and the tone of the black improved by heating the dyed yarn for 30 mins. at 60° with the following emulsion: 5 p.c. of soap, 1·5 p.c. of olive oil, and 1·0 p.c. of ammonia in 2 litres of water. The finished yarn is then squeezed out and dried without washing.

The dyeing process for Vidal black (*P.*) from p-nitrophenol is carried out as above with 10–15 p.c. of the colour, but in this case, after-chroming is essential in order to develop the full shade of black from the dark green tints produced by aerial oxidation. The above-described finishing process enhances the tone of black obtained by chroming.

Immedial black V extra (*C.*) is dyed in full shades with 15–25 p.c. of colour, 10–18 p.c. of crystallised sodium sulphide, and for each 10 gallons of liquor are added 4·5–8 oz. of sodium carbonate and 1–3 lbs. of common salt or anhydrous sodium sulphate. The yarn is dyed at a boiling temperature for 1–1½ hours and rinsed in water, containing 4·5–8 oz. of sodium formate or acetate per 10 gallons of liquor. For grey shades only 1–8 p.c. of this black is required, with 2–6 p.c. of sulphide crystals, one-third the amount of salt or sodium sulphate, and the same proportion of sodium carbonate as for full black shades.

Thiogene black conc. (*M.*) and thioxine black RNO (*O.*) are dyed in full shades with 10 p.c. of colour, 30 p.c. of crystallised sodium sulphide, 8–10 p.c. of dry sodium carbonate, and 50 p.c. of common salt or anhydrous sodium sulphate. The bath should have at 15° a sp.gr. of 6·7°Be. Cotton yarn is dyed at the boil for 1 hour, and mercerised yarn at 90° for a somewhat longer period.

An increase in fastness and depth of the sulphide blacks is produced by an after-treatment with 1–2 p.c. of chrome alum or copper sulphate, 1·5–2 p.c. of potassium bichromate, and 5 p.c. of acetic acid.

Sulphide blues. Immedial indone 3B is dyed on cotton yarn in pale and medium shades by using 2–10 p.c. of colour, 5–20 p.c. of sulphide crystals, and 2–10 p.c. of glucose with 4·5–8 oz. of soda ash and 1 lb. of common salt or dry sodium sulphate to each 10 gallons of water. Deeper shades are obtained with 10–16 p.c. of colour, and correspondingly greater amounts of sodium sulphide and glucose. The lighter shades are dyed at 30°–40°, and the darker at 60°–80°, a brighter tone being thus obtained than at the boiling temperature.

Thiogene deep blue and thiogene cyanine B are dyed in full shades with 6–10 p.c. of colour, 10–15 p.c. of sulphide crystals, 5 p.c. of sodium carbonate, and 30 p.c. of sodium chloride at a boiling temperature for 1 hour.

Sulphide greens. Immedial green is dyed on cotton in full shades with 14 p.c. of colour, the same proportion of sulphide, 0·5 p.c. of soda ash, and 5 p.c. of common salt or dry sodium sulphate. The tint is brightened by exposure to air after rinsing, or by warming the dyed yarn with soap solution containing sodium carbonate.

Sulphide yellows. Thiogene yellow 5G and thioxine yellow G require for the dyeing solution from 2 to 4 times their weight of sulphide crystals; the bath is prepared with 4–5 p.c. sodium carbonate, 25–35 p.c. of sodium chloride, or 15–20 p.c. of dry sodium sulphate, the dyeing being effected just below the boiling-point. Immedial yellow GG is dyed at 70°–80° without sodium chloride or sulphate.

Sulphide browns. These colouring matters dissolve with 0·4–1·0 part by weight of sulphide crystals, and are dyed for 1 hour at the boil with sodium carbonate and sodium chloride, full shades being obtained with 8–10 p.c. of colour. The fastness of sulphide browns to light, washing, milling, and alkalis is very satisfactory, but they are appreciably affected by chlorine or hypochlorites.

Sulphide violets and purples. The maroons, violets, purples, and bordeaux of this series are best dyed at 60°–80°, and not at boiling temperatures. In some cases sodium chloride or sulphate is not added to the bath, but a little glue (one-fifth of the weight of dye) is introduced with the object of brightening the shade.

Sulphide colouring matter as vat dyes. Immedial blue is reduced with alkaline hydrosulphite until the solution assumes a brownish-yellow colour, the cotton is then introduced, and the colour developed on the fibre by oxidising agents. Indigo can be dyed from the same bath. The sulphide dyes cannot be employed in the zinc-dust or alkaline ferrous sulphate vat, because they yield insoluble lakes with the metallic radicles present (*M.* D. R. P. 146797; Eng. Pat. 24455, 1899; Fr. Pats. 295589, 301740; U. S. Pat. 680472; *cf.* Fr. Pats. 299733, 385087).

Various brands of sulphide black (*e.g.* kryogen black and thiophenol black) have been dyed on cotton from a fermentation vat, although the process is unserviceable for the animal fibres (*B.* D. R. P. 200391; Eng. Pat. 12219, 1907; Fr. Pat. 379584).

Dyeing of sulphide dyes on wool, silk, and fibres other than cotton. The destructive action of the alkali sulphide on wool and silk is mitigated by adding to the dye-bath an amount of dextrose equal to twice the weight of sodium sulphide present. Silk is dyed for 1 hour at 80° in 20 times its weight of liquor, each litre of which contains 20–30 grms. of sulphide black, or 5–10 grms. of some other sulphide colour, 1 grm. of sodium carbonate, 5–10 grms. of Glauber salt, 3 c.c. of turkey-red oil, and the minimum amount of sodium sulphide with twice its weight of dextrose (*C.* D. R. P. 161190).

Wool is dyed at 60° in a similar bath, but without the turkey-red oil. Tannin may be employed as the protective agent instead of dextrose. A preliminary treatment of wool with warm 4 p.c. formaldehyde solution protects the fibre from the action of alkali sulphides (Kann, D. R. PP. 144485, 146845; Eng. Pat. 25971, 1906); but wool thus treated, although taking up sulphide dyes (*e.g.* cachou de laval) in moderately alkaline baths at 90°, is not dyed by sulphide colours in colder baths of moderate alkalinity (Levinstein, J. Soc. Dyers. 1907, 296; Eng. Pats. 25971, 1906; 19840, 1907). The addition of ammonium chloride or alkali bisulphite lessens the destructive action of alkali sulphides on wool and silk (*Bl.* D. R. P. 130848).

Artificial silk is readily dyed by sulphide colours even at comparatively low temperatures, 30°–40°, for light shades, and 60° for heavy shades, in the latter case the bath being prepared with sodium sulphate and sodium carbonate. Ramie and hemp fibres are readily dyed by sulphide colours, jute absorbs these dyes less easily than the cotton fibre.

CONSTITUTION OF SULPHIDE DYES.

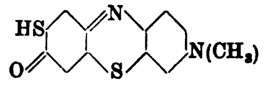
The problem of ascertaining the constitution of the sulphide dyes is greatly complicated by the uncrystallisable nature of these products, and by the circumstance that these dyes, like many other substantive colours, tend to form colloidal solutions which render impossible the determination of their molecular weight.

Only in the case of the simplest members of the series, the sulphide blues, has it been found possible to obtain crystalline derivatives, and through these compounds to establish a relationship between the sulphide blues and the colours of the methylene blue series.

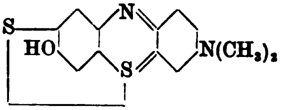
Immedial pure blue (*C.* D. R. P. 134947) gives a bisulphite compound

$$C_{14}H_{12}O_4N_2S_3,NaHSO_3,2H_2O,$$

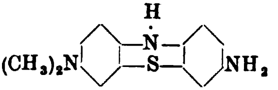
crystallising in yellow needles (D. R. P. 135952). The colouring matter contained in this additive compound has been given the following constitution, but probably immedial pure blue is the disulphide corresponding with the mercaptan represented by the first of these formulæ



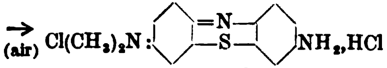
or



Gnehm and Bots (J. pr. Chem. 1904, [ii.] 69, 169) find, however, that the bisulphite compound is more correctly represented by the formula $C_{14}H_{12}O_2N_2S_3,NaHSO_3,2H_2O$, a result which would indicate a somewhat different constitution for immedial pure blue. On heating methylene blue with alcoholic ammonia at 140° Gnehm and Kaufler (Ber. 1906, 39, 1016) obtained dimethylleucothionoline I.

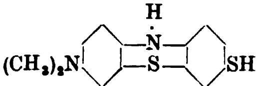


I.

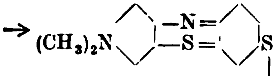


II.

which became oxidised to dimethylthionoline (II.). The diazo compound of the latter was converted into the corresponding xanthate, and this substance hydrolysed with 80 p.c. sulphuric acid. The final product was an amorphous bluish-black powder, dissolving in aqueous sodium sulphide to a colourless leuco compound, and dyeing cotton from this solution in greyish-blue shades. These results indicate that the replacement of NH_2 in dimethylleucothionoline by SH furnishes a leuco compound, having the constitution III., and accordingly the bluish-black substance, which has the properties of a sulphide dye, would probably be represented by the formula IV.

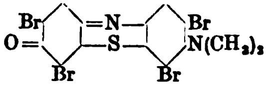


III.



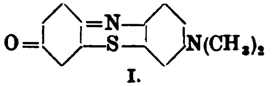
IV.

Moreover, immedial pure blue, when heated in sealed tubes with potassium chromate and hydrobromic acid, gives a 42 p.c. yield of etrabromomethylene violet

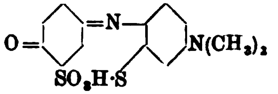


a substance which has also been produced synthetically from methylene blue (Gnehm and Kaufler, Ber. 1904, 37, 2618, 3032).

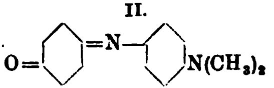
Methylene violet (I.) and the indophenolthiosulphonic acid (II.), when treated below 140° with sodium tetrasulphide in aqueous or alcoholic solution, yield a blue closely analogous to immedial pure blue which is prepared from the indophenol (III.)



I.



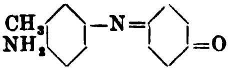
II.



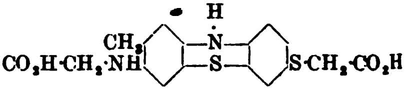
III.

The similarity in the products of these two condensations points to the existence in the sulphide blues of the thiazine ring, which is present in methylene blue, but in addition the leuco derivatives of sulphide blues contain SH groups, which undergo oxidation to insoluble sulphide blues, which are to be regarded as complex disulphides.

Immedial indone, produced from the indophenol

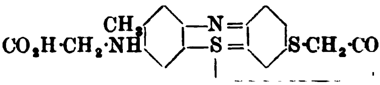


has been found by Frank to undergo condensation with chloroacetic acid, so that its leuco derivative gives rise to a readily purified compound containing two $CH_2{\cdot}CO_2H$ groups

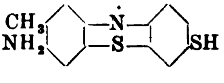


(Chem. Soc. Trans. 1910, 97, 2047).

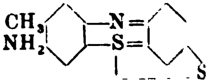
This product is readily oxidised to a blue colouring matter, which, unlike the original immedial indone, has no affinity for cotton in a sodium sulphide bath, but dyes wool bright blue from an acid bath. This wool dye has very probably the following constitution—



These results, therefore, indicate that the constitutions of leuco-immedial indone (I.) and of immedial-indone (II.) are most probably to be represented respectively by the following formulæ—



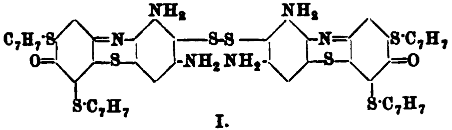
I.



II.

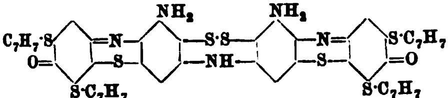
The alkylation of immedial black with benzyl chloride in the presence of aqueous sodium sulphide leads to the production of several substances which are separated by successive extraction with carbon disulphide, chloroform, and phenol and chloroform (D. R. P. 131758).

The substance soluble in carbon disulphide has the empirical formula $C_{52}H_{40}O_2N_6S_8$, and is regarded as having the following constitution (I.)—



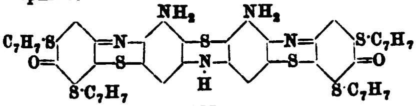
I.

A second product (II.), sparingly soluble in carbon disulphide, and extracted by chloroform, results from the foregoing by the elimination of ammonia.



II.

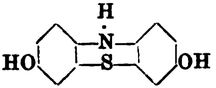
A third substance, insoluble in carbon disulphide and chloroform, is produced by eliminating ammonia from 2 molecules of the first product; and a fourth compound (III.), differing from the first in containing less sulphur and less nitrogen, has also been isolated, being sparingly soluble in chloroform, although insoluble in carbon disulphide.



III.

These results serve to indicate the relationship between the more complex sulphide blacks and the less condensed sulphide blues. They show, moreover, that in all probability the blacks are not homogeneous compounds, but mixtures of highly-condensed molecules (*cf.* Ris, Ber. 1900, 33, 796; D. R. P. 122850).

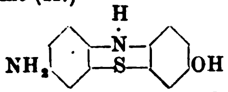
Vidal's earlier researches also point to the existence of thiazine rings in sulphide blacks (Mon. Scient. 11, 2, 655; 17, 427; D. R. P. 99039). On heating together quinol, sulphur, and ammonia, water and hydrogen sulphide were eliminated and leucothionol (I.) was produced



I.

which is also formed together with a large proportion of black colouring matter by heating *p*-aminophenol and sulphur, and is obtained in quantitative yield by heating molecular proportions of *p*-aminophenol and quinol with sulphur.

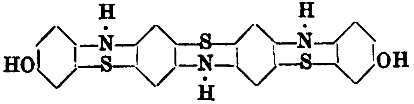
Quinol and *p*-phenylenediamine, when heated with sulphur, give water, hydrogen sulphide, and leucothionoline (II.)



II.

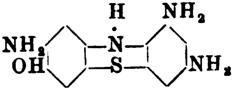
which on further heating with sulphur gives a black colouring matter.

Since leucothionol, on heating with sulphur and ammonia, also gives rise to a black dye, Vidal supposes that the black arises from a further condensation of leucothionol and leucothionoline to form dihydroxytetraphentrithiazine



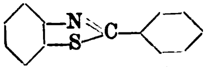
which he regards as being the essential constituent of Vidal black. This assumption does not, however, explain the characteristic mercaptan properties of the sulphide colours. It is evident that these colours must, in addition to the thiazine rings, contain mercaptan sulphur SH, or even polysulphide sulphur S_xSH in side chains.

2 : 4-Diaminophenol is readily converted by aqueous sodium polysulphide at 100° into diaminoleucothionoline



which is easily oxidised to the corresponding diaminothionoline, but without exhibiting any dyeing properties. When, however diaminophenol is heated with aqueous thiosulphate, it passes into complex thiosulphonic derivatives, dissolving in aqueous alkalis to blue solutions, and dyeing cotton in blue shades. In the second thionation of diaminophenol, sulphur is introduced into the side chain as well as into the thiazine ring. The processes for preparing Clayton black are further examples of this type of condensation (D. R. PP. 106036, 120504, 120560, 136016; Eng. Pats. 21832, 22460, 1898; Fr. Pat. 288465).

The yellow and brown sulphide dyes resemble dehydrothiotoluidine and primuline in containing the thiazole group



characteristic of the latter substances, and for this reason they are largely produced from tolylene-2 : 4-diamine, tolidine, and similar compounds containing carbon in side chains.

The sulphur of the thiazole ring is introduced by direct interaction of this element and the organic substance, giving rise to an insoluble coloured product which is rendered soluble by subsequent treatment with hot concentrated aqueous sodium sulphide. In the latter operation, mercaptan (hydrosulphide) groups are introduced into the molecule of the coloured substance, with the result that a true sulphide dye soluble in alkali sulphide solution is produced.

Bibliography.—Friedländer, Die Fortschritte der Teerfarben-fabrikation (-industrie); Lunge, Die Schwefelfarbstoffe, Leipzig, 1912; Nietzke, Chemie der Organischen Farbstoffe; Schultz und Julius, Tabellarische Uebersicht der Kunstlichen Organischen Farbstoffen. G. T. M.

SULPHINE *v.* Primuline and its derivatives.

SULPHOCYANIDES or **THIOCYANATES** *v.* Cyanides.

SULPHONAL *diethylsulphonedimethylmethane* $(CH_3)_2C(SO_2C_2H_5)_2$ was first prepared by Baumann by treating dithioethyldimethyl methane or acetone mercaptol

$(CH_3)_2C(SC_2H_5)_2$

with 5 p.c. potassium permanganate solution (Ber. 1886, 19, 2808).

It may also be prepared by heating diethyl sulphone methylene methane $MeCH(SO_2C_2H_5)_2$ or diethylsulphonemethane $CH_2(SO_2C_2H_5)_2$ with alcoholic potash and methyl iodide (Fromm, Annalen, 1889, 253, 147).

Some difficulty is experienced in preparing an odourless product. According to Kobbe, it is easy to determine whether a preparation is odourless or not by boiling 1 grm. with about 10 c.c. of water in a test tube, when any remaining odour is easily detected (Kobbe, Pharm. Zeit. 1888, 730).

To isolate sulphonal from mixtures containing it, the mixture is evaporated to dryness, extracted 3 times with its own volume of 90 p.c. hot alcohol, the extract on cooling is filtered and the alcohol distilled off. The residue is filtered while still hot, a few drops of potash added to the filtrate and treated 3 times with 3 times its volume of ether. The ether is then evaporated, the residue is dissolved in water and again treated with ether; on evaporation pure sulphonal is left (Vitali, Boll. Chim. Farm. 39, 461, 497).

Sulphonal forms colourless, odourless, almost tasteless prismatic or elegant foliated crystals. It may be identified as follows: it melts at 125·5°, volatilises at 300°, dissolves in 15 parts of boiling water, and 500 parts of water at 15°; in 133 parts of ether at 15°; 2 parts of boiling alcohol, 65 parts of alcohol at 15°; and in 110 parts of 50 p.c. alcohol at 15°. 100 c.c. of benzene dissolve 8·01 grms., 100 c.c. of petroleum spirit 0·06 grms., and 100 c.c. of chloroform 32·5 grms. Toluene and acetone also dissolve considerable quantities of sulphonal. The sample should also be tested for sulphuric acid, potassium, and manganese. It is exceedingly inert towards all reagents, a characteristic property of the substance. Fused with potassium cyanide, it gives a smell of mercaptan. Mercaptan, according to Ritsert, may be formed by heating sulphonal with sodium-amalgam or pyrogallol. Fused with dry potash, a smell of mustard oil is evolved. Mercaptan is also formed by heating the substance with zinc chloride, sodium acetate, manganese dioxide, sodium amalgam, or with a fragment of charcoal; the white fumes which are at the same time given off turn litmus-paper red, and decolorise blue iodide of starch paper (J. Soc. Chem. Ind. 1888, 772; Kippenberger, Zeitsch. Nahr. Genussm. 1899, 2, 75). These tests, however, are said to be given by other compounds containing sulphur.

By the following method 0·001 grm. may be detected. When sulphonal is heated moderately with 3 times its weight of powdered potash, an unpleasant smell is developed, the liquid becoming first yellow, then red, it becomes scarlet on cooling and changes to blue on addition of water, the liquid becoming turbid. On filtering and adding hydrochloric acid to the filtrate, the latter becomes violet, sulphur dioxide is evolved and sulphur is precipitated. In the residue obtained by evaporating the acid solution to dryness, sulphate, hyposulphite and polysulphide may be detected in the usual way.

If the original mixture of sulphonal and potash be heated very strongly the red coloration changes to blue (Vitali, *l.c.*).

Sulphonal may be detected in trional and tetronal by treating the sample with ether in which sulphonal is much less soluble than the other two substances. The undissolved residue, if it contains sulphonal, can be detected by its m.p. 125·5°, its characteristic crystalline form and other reactions (Gabutti, J. Pharm. Chim. 1907, 25, 183).

Sulphonal is employed as a hypnotic, being intermediate in its action between chloral and paraldehyde and much safer than most drugs of its class as it does not depress the heart (Fischer, Pharm. Zeit. 33, 235).

Chlorsulphonal $CH_3(CH_2Cl)C(SO_2C_2H_5)_2$ forms white pearly crystals, m.p. 78°–79° (Autenrieth, Ber. 1891, 24, 171).

Nitrososulphonal $CH_3(CH_2{\cdot}NO)C(SO_2C_2H_5)_2$, rhombic tablets, has m.p. 104°–105° (Posner, *ibid.* 1899, 32, 1246).

Trimethylpiperidinediethylsulphonal

$$(C_2H_5SO_2)_2C{<}\begin{matrix}CH_2{\cdot}CH(CH_3)\\CH_2{\cdot}C(CH_3)_2\text{-}\end{matrix}{>}NH$$

is obtained by oxidising the corresponding mercaptol with potassium permanganate in dilute sulphuric acid (Pauly, *ibid.* 1898, 31, 3149). It forms lustrous feathery crystals, m.p. 135°.

Sulphonal carboxylic acids are described by Posner (Chem. Zeit. 1905, 29, 1107).

Compounds in which the C_2H_5 group is replaced by some other radicle are formed from the corresponding mercaptan by similar methods to those used for preparing sulphonal (Stuffer, Ber. 1890, 23, 3228) (*v.* KETONES, also SYNTHETIC DRUGS).

SULPHONATED OILS (Turkey-red Oils), *v.* OILS, FIXED, AND FATS.

SULPHONES $\begin{matrix}R\\R_1\end{matrix}{>}SO_2$ may be obtained by oxidising vigorously the thioethers, or the sulphoxides, or the sulphides (Beckmann, J. pr. Chem. [ii.] 17, 439; Baumann and Walter, Ber. 1893, 26, 1124); by washing an alcoholic solution of sodium sulphinate or sodium alkylsulphinate with alkyl or alkylene halides (Otto, Ber. 1880, 13, 1272; *ibid.* 1888, 21, 652, 658; Annalen, 1894, 283, 181; *ibid.* 1895, 284, 300; Michael and Palmer, Amer. Chem. J. 6, 253) by the action of sodium alkyl sulphinate or mercaptide on chloracetone thus:

$$CH_2Cl{\cdot}CO{\cdot}CH_3+SO_2PhNa$$
$$=NaCl+SO_2Ph{\cdot}CH_2{\cdot}CO{\cdot}CH_3$$

(Otto and Rössing, Ber. 1890, 23, 752); by the action of phosphoric anhydride at a high temperature on a mixture of an aromatic sulphonic acid and a hydrocarbon (Michael and Adair, *ibid.* 1877, 10, 583; *ibid.* 1878, 11, 116); by the interaction of an aromatic sulphochloride and a hydrocarbon in the presence of aluminium chloride $RSO_2Cl+R'H=HCl+RR'SO_2$ (Beckurts and Otto, *ibid.* 2066); by the interaction of aromatic sulphinic acids and halogen derivatives of aromatic nitro compounds (Ullmann and Pasdermadjian, Ber. 1901, 34, 1150); a sulphone of formula $C_6H_5SO_2C_{10}O_7$, m.p. 121°, has been obtained by heating benzene sulphonic chloride with naphthalene and zinc dust (Chrustschoff, Ber. 1874, 7, 1167) and di-*p*- and di-*o*-xylyl sulphones have been prepared by subjecting the well-cooled xylene to the action of sulphuric anhydride (Zorn and Brunnel, Compt. rend. 1894, 119, 1224).

For other methods, *see* Otto, Ber. 1885, 18, 154, 246; *ibid.* 1891, 24, 1832; Stuffer, *ibid.* 1890, 23, 3226; Damköhler, J. pr. Chem. [ii.] 30, 321; Genvresse, Bull. Soc. chim. 1894, [iii.] 11, 501; Eng. Pat. 16333; J. Soc. Chem. Ind. 1899, 980; Blanksma, Pr. K. Akad. Wetensch. Amsterdam, 1901, 4, 264; Posner, Ber. 1905, 38, 646.

The sulphones are isomeric with the organic alkyl sulphinates $R{\cdot}SO{\cdot}OR$, and form stable, neutral solid bodies not attacked by nascent hydrogen, hydrogen iodide, or by phosphorus pentachloride.

The sulphones of general formula $R_2C(SO_2R)_2$ are stable towards alkalis, but when one of the groups SO_2Ph, SO_2Et, or Cl is introduced, they are decomposed by alkalis, the three sulphone groups being eliminated as sulphinic acid (Autenrieth, Ber. 1891, 24, 1512; Stuffer, *ibid.* 1890, 23, 1408). Diphenyl sulphone, when heated with sulphur at 250°–275° in a current of carbon dioxide, yields diphenyl sulphide, but many other sulphones do not react thus (Böeseken, Rec. trav. chim. 1911, 30, 137).

Sulphones containing one benzyl and another aromatic residue react with formaldehyde yielding diformal derivatives, but the presence of two aromatic residues without a benzyl group, or a benzyl group without a second aromatic residue, hinder this reaction (Fromm and Erfurt, Ber. 1909, 42, 3823).

Some of the disulphones $R_2C(SO_2R)_2$ are employed in medicine (*v.* SULPHONAL, TRIONAL, TETRONAL). According to Baumann and Kast (Zeitsch. physiol. Chem. 14, 52; *ibid.* 1889, 15, 32; *see* also Laves, Arch. Pharm. 229, 448), the SO_2 group as such has no hypnotic effect and the sulphones containing the ethyl group are the most powerful, the methyl group having little or no effect.

But in the case of dimethyl sulphone dimethyl methane $Me_2C(SO_2Me)_2$, the replacement of the methyl by the ethyl group produces no alteration in physiological properties, whilst the propyl, and to a less extent the *iso*-propyl, increases the activity. On the other hand, the introduction of a carbonyl group as in 2:2-diethyl sulphone pentane-3-one

$$CMe(SO_2Et)_2COEt$$

destroys the hypnotic and all noxious properties (Hildebrandt, Chem. Zentr. 1905, ii. 502). The influence of other groups has also been studied by Hildebrandt.

SULPHONIC ACIDS $R{\cdot}SO_3H$. These acids may be conveniently described under two headings: (*a*) aliphatic sulphonic acids, (*b*) aromatic sulphonic acids.

Aliphatic sulphonic acids. These acids are not of much importance.

General methods of preparation. (i.) By the oxidation of mercaptans, alkyl disulphides, or alkyl thiocyanates with nitric acid.

(ii.) Their salts and esters are formed by the interaction of alkyl iodides with alkali sulphite and silver sulphite and the required alcohol respectively.

(iii.) By the oxidation of sulphinic acids.

Properties. They are mostly viscous liquids, readily soluble in water, and usually can be obtained crystalline. On heating they undergo decomposition; by fusion with caustic alkalis they are decomposed into alcohols and alkali sulphites, but they remain unchanged when boiled with aqueous alkali hydroxides. Phosphorus pentachloride converts them into sulphonic chlorides.

Aromatic sulphonic acids. These acids are easily obtained by digesting the substance to be sulphonated with sulphuric acid. The number of hydrogen atoms replaced depends on the strength of the acid and on the temperature. These acids are important as the source of many dyes; many dyes which are insoluble in water are converted into their sulphonic acids which are readily soluble. The aromatic sulphonic acids are also manufactured to be converted into phenols by fusion with caustic alkali. Many are also valuable as synthetic drugs (*q.v.*).

General methods of preparation. (i.) By digesting the substance with sulphuric or anhydrosulphuric acid; or with chlorosulphonic acid when the sulphonic chloride is produced.

(ii.) By the oxidation of thiophenols or of sulphinic acids.

(iii.) By heating diazoamino compounds with sulphurous acid.

Of these methods the first is the most important. It is often somewhat difficult to isolate the acids, as they are readily soluble in water, are non-volatile, cannot be extracted from aqueous solutions with organic solvents or separated from other substances by steam distillation. The following method is usually employed: excess of sulphuric acid is removed from the sulphonation product by boiling with excess of barium carbonate; the precipitated barium sulphate is filtered off, and to the filtrate which contains the barium salt of the sulphonic acid, sulphuric acid is added until precipitation no longer occurs. After filtering, the solution is evaporated to dryness when the acid is obtained either crystalline or as a syrup. Calcium carbonate may be used instead of barium carbonate, in which case, as the acid will contain a little calcium sulphate, alcohol is added to the final product, the calcium sulphate filtered off, and the alcohol removed by evaporation. Sometimes lead carbonate is employed, when the lead salt of the sulphonic acid is decomposed with hydrogen sulphide. These methods only apply when the barium, calcium, or lead salts are soluble in water.

When two or more sulphonic acids are present, separation is usually effected by fractional crystallisation of their salts. If this is not effectual, they are converted into sulphonic chlorides by means of phosphorus pentachloride. The sulphonic chlorides are well-defined crystalline substances, which can easily be obtained in a pure state.

Properties. The aromatic sulphonic acids are usually very soluble in water, and when obtained crystalline, are often very hygroscopic. They can be salted out from aqueous solutions as sodium salts by the addition of sodium chloride. They gradually decompose when heated, so seldom have a definite melting-point. They are strongly acid substances, decomposing carbonates and dissolving certain metals with evolution of hydrogen. The following are the principal reactions in which they take part:—

(i.) Phosphorus pentachloride or oxychloride converts their alkali salts into *sulphonic chlorides.*

(ii.) Fusion with caustic alkalis yields *phenols.*

(iii.) Distillation with potassium cyanide yields *nitriles.*

(iv.) *Hydrocarbons,* together with *phenyl sulphones,* are formed by distillation of the acids alone or with hydrochloric acid.

(v.) The sulphonic group may be replaced by the *nitro group* by the action of nitric acid.

(vi.) The sulphonic group may be replaced by the *amino group* by the action of sodamide.

(vii.) The sulphonic chlorides are converted into *thiophenols* on reduction.

SULPHUR. Sym. S. At.wt. 32·07. This substance has been known from the earliest times. Its ancient and familiar name of brimstone (A.S. *byrnan,* to burn, and *stane,* a stone, probably corrupted from *brinstone* or *brenstone,* *i.e.* fiery stone) is based upon the circumstance that it is combustible and that, when ignited, it will continue to burn in presence of air with a characteristic blue flame until it is entirely consumed. To the alchemists the term sulphur was practically synonymous with the principle of inflammability, and hence was not necessarily restricted, as now, to the element.

Sulphur occurs in the free state in the neighbourhood of volcanos, active and extinct, and is a characteristic product of volcanic action. Volcanic sulphur is found largely in Italy, Sicily, Iceland, Mexico, North and South America, Japan, Asia, New Zealand, and other parts of the world, and some of these places constitute valuable sources of supply.

Deposits of free sulphur occur in sedimentary rocks as a product of bacterial action, certain bacteria having the property of reducing sulphates and of assimilating sulphur to a relatively large extent. In union with a great variety of metals sulphur occurs as *sulphides,* and some of these compounds constitute important metalliferous ores. Combined with oxygen and bases, sulphur is found in nature as *gypsum, selenite* and *anhydrite* (calcium sulphate); as *heavy spar* (barium sulphate); as *celestine* (strontium sulphate); as *Epsom salts* and *kieserite* (magnesium sulphate), etc.

Sulphur is also found in nature combined with hydrogen, as *hydrogen sulphide* or *sulphuretted hydrogen,* and occasionally with carbon and oxygen as *carbon oxysulphide* in a number of mineral waters which are supposed to owe their therapeutic value to such sulphur compounds.

Sulphur is found unoxidised, but combined, in vegetable and animal tissues, in a variety of proteid substances; in the hair, nails and horn; in the taurin of the bile, in the cystine in urine, &c. Many volatile oils, *e.g.* oil of mustard, oil of garlic, &c., are composed of organic sulphur compounds to which their characteristic smell and other properties are due.

For many years past, and until the year 1903, about 95 p.c. of the world's supply of sulphur was mined and prepared for use in Sicily, the greater portion of the remainder being obtained from Romagna, in Italy, and from Japan. But the successful application of the Frasch process, a description of which follows, to the winning of pure sulphur at a low cost from deposits at Calcasieu Parish in Louisiana, U.S.A., long known but unworkable by ordinary mining methods, has resulted in a reduction at the end of 1912 of sales of Sicilian sulphur from the 95 p.c. per annum of the world's consumption above mentioned to about 50 p.c.

In the year 1900 the production in the United States was about 2000 tons. After the Frasch process was developed upon a practical scale during the year 1902 the production increased to 30,000 tons; in 1903, to 137,292 tons; and the production in 1913 is upwards of 300,000 tons per annum. All the requirements of the United States are met by Frasch sulphur with the exception of Japanese sulphur supplied to the western coast, and the imports from Sicily have fallen until they may now be regarded as negligible. The exports from the United States of Frasch sulphur have thus far not been developed to any great extent, but since 1905 about 30,000 tons have been sent annually from Louisiana to France. Having regard to the stocks now accumulated, to the vast tonnage of obtainable sulphur stated to be in sight, and to the extremely low cost of winning sulphur of great purity as compared with the methods employed in Sicily, it would appear that should it be considered desirable to extend the export trade of Frasch sulphur there is no reason why it should not be done upon a very large scale.

The Frasch process has proved to be applicable to the extraction of sulphur from the deposits in the dome formations of the Gulf Coastal-Plain regions, of which the deposits at Calcasieu in Louisiana constitute a portion. Other deposits have been located in this formation, and it is stated that a very important one in Texas at Bryan Hill, about forty miles from Galveston, is about to be worked upon a large scale by the Freeport Sulphur Company, and that a modification of the Frasch superheated steam process is to be employed.

Sulphur deposits in other parts of the world are now well known, and in addition to those already named may be mentioned those in the Caucasus, in Jebels Kabrit and Jemsah in Upper Egypt, and on White Island in New Zealand.

Japanese sulphur is of high purity and has a market to the extent of about 30,000 tons per annum. Of the total output, about 90 p.c. is obtained from the deposits which have been worked for many years in the volcanic district of Central Hokkaiedo. It is mainly shipped to the Pacific ports of the United States and to Australia. The sulphur is of what is known as the soltafara type and is deposited in cracks in the lava and in the tuffs owing to the interaction of sulphuretted hydrogen and sulphurous acid gases which have their origin in active or expiring volcanos.

Italian sulphur. Between 30,000 and 40,000 tons of sulphur are obtained per annum from deposits in Romagna which have long been worked. The sulphur thus obtained is almost exclusively employed in Italy for agricultural and viticultural purposes.

Sicilian sulphur is stated to have been employed in industry during the past 300 years. It is estimated that about 16,000,000 tons have been mined and extracted up to date, and until the introduction of Louisiana sulphur, extracted by the Frasch process, Sicily controlled the sulphur industry of the world.

The sulphur occurs in Miocene strata and constitutes what is known as the 'gypsum' type as distinct from the 'soltafara' type. Marls, shale and gypsum are prominent constituents of the sedimentary rocks in which the sulphur is produced. The reducing action of the bituminous matter under efficient conditions of temperature and pressure upon gypsum results in the formation of calcium sulphide, which in turn is acted upon by oxygen, carbonic acid and moisture, producing calcium carbonate, sulphuretted hydrogen and polysulphide of lime. The latter in turn yields calcium carbonate, sulphur and sulphuretted hydrogen. It is stated by Fuchs and De Launay (Traité des Gites Mineraux, p. 274) that 24 p.c. of sulphur would represent about the average that would be deposited as the result of these reactions, and inasmuch as this percentage may be taken as representing the average amount of crude sulphur found in Sicilian sulphur rock, it is regarded as a strong argument in favour of the sulphur being deposited in the manner suggested.

The mines are distributed throughout the provinces of Caltanisetta and Girgenti. They cover an area of about 100 miles by about 55 miles. The deposits of sulphur (*solfare*) vary in depth from 150 ft. to about 650 ft., and in the deep mines the ore is now all brought to the surface by mechanical means: in the past it was practically all dealt with by manual labour.

The ore varies very considerably in its total sulphur contents. The rich ore contains from 30 p.c. to 40 p.c. of crude sulphur, which, depending upon the method of extraction employed, yields from 20 p.c. to 25 p.c. of commercial sulphur. But the average ordinary ore contains from 20 p.c. to 25 p.c. and yields from 10 p.c. to 15 p.c. of commercial sulphur. In some ores the sulphur is as low as 8 p.c., but unless they contain about 15 p.c. they do not pay for working by the method adopted in Sicily.

In addition to the 16,000,000 tons which have been stated to have been mined, prepared and sold, it has been officially reported by a highly qualified engineer that the quantity of commercial sulphur still in sight in the Sicilian deposits amounts to about 34,000,000 tons.

The effect of the Louisiana sulphur competition upon Sicilian production may be strikingly illustrated by the fact that in the year 1903 there were 757 active sulphur mines in Sicily and that nearly 40,000 operatives were employed. To-day the number of mines being worked is about 400 and the number of operatives about 20,000.

It must be admitted that the methods of extracting sulphur employed in Sicily were not adapted to meet competition of a serious character, although it should be equally admitted that substantial progress has been made since the regenerative furnace has been brought to its present stage of development. Since 1850 the method mainly employed was to submit the ore containing not less than 15 p.c. of sulphur to combustion, the necessary fuel being mainly provided by the sulphur itself, about one-quarter of which was thus consumed. When this process is employed the ore is massed in large quantity in circular heaps of about 60 ft. diameter and about 9 ft. deep. The heaps are coated externally with moistened ash obtained from the burnt ore. Each heap is provided internally with a sloping floor fitted with compartments in which the fused sulphur produced by the heating collects and from which it is subsequently recovered in the form of loaves weighing about one hundredweight each. The heaps thus prepared are known as *calcaroni*. The process is started by charging in wood fuel from the top of the heap and setting fire to it, and this heat is maintained by means of lighted wood. By this process the loss of sulphur by combustion is so considerable that the yield of sulphur obtainable as loaves is only about 60 p.c. of the total sulphur contained in the ore. In addition to the large loss of sulphur thus occasioned, the pollution of the atmosphere is very great, and where the *calcaroni* system has been worked upon a continuous large scale, much damage has been caused to the trees and plants in the surrounding country.

In 1880 Robert Gill introduced his regenerative furnace into Sicily, and it has since been improved and developed very considerably. The object of its construction was to effect the easy regulation of the combustion and to provide a continuous process. In order to effect this, two large square brick furnace chambers, provided with double floors on which the molten sulphur collects and subsequently cools and solidifies, are independently connected with a chimney stack, and the heating of the chambers is so regulated that when the ore has been treated in one chamber the heating of the other chamber is at once started, and therefore the process becomes continuous. But still greater improvements have been effected by the provision of as many as six large circular chambers connected with the chimney instead of the two square chambers above-mentioned, and these have been still further improved by combustion air regulating devices which are found in the Sanfilippo furnaces now mainly employed in Sicily. By this method the extraction of sulphur from the ore can be effected up to about 80 p.c., a very great advance upon the yield obtainable from the *calcaroni*, which have now been substantially superseded.

Serious attempts have also been made in Sicily to extract sulphur by means of superheated steam under pressure, and in this way it has been found possible to obtain a yield of sulphur as high as 90 p.c. of that present in the ore. But steam extraction, although successfully applied in Romagna, would not appear to be practicable upon a large industrial scale in Sicily owing to the cost of fuel and the losses occasioned when much gypsum is present, as is often the case.

It is difficult to arrive at an absolutely accurate figure as regards the present cost of sulphur production in Sicily, but it would appear that the position may be fairly summed up by stating it at 40*s*. per long ton, and this is probably placing the figure too low. This price of Sicilian sulphur production must undoubtedly be carefully taken into consideration when making a comparison between the future industrial possibilities of Sicilian sulphur and those of other deposits which have been referred to.

The commercial crude Sicilian sulphur, which constitutes a very large proportion of the island sulphur trade, contains impurity ranging in amount from about 2 p.c. to about

11 p.c. It is known as *Greggio*, and its price varies according to the amount of impurity. Thus it is graded as 'Best Unmixed Seconds,' 'Best Unmixed Thirds,' and 'Current Thirds.' These three qualities practically represent the entire Sicilian brimstone trade. The difference in price between the best and worst qualities is about 5*s.* per ton, and if pure sulphur be required it is prepared by refining and as a result the impurity of the commercial refined product is reduced to about one-half p.c. It is then sold as *Raffinate*.

In its preparation the crude sulphur is subjected to sublimation and one of two different kinds of product may be prepared. If the temperature of the condensing chamber is kept well above 100°C. then the molten sulphur is allowed to flow into moulds and when solidified is sold as refined sulphur. If the temperature is kept below 100°C. then flowers of sulphur are formed, for which there is a very considerable industrial demand. When sulphur is used for application to vines, the crude sulphur is ground so as to pass through fine mesh sieves, or it may be preferably winnowed by means of compressed air. When thus treated the sulphur is found to adhere to the foliage of the vine, whereas if it be sublimated and condensed it will not satisfactorily adhere.

The history of the Sicilian sulphur industry is characterised by the remarkable changes to which it has been subjected. Previous to the year 1838, sulphuric acid, wherever manufactured, was made from brimstone, and the supply came practically from Sicily only. It is thus apparent that the alkali industry was, to a great extent, dependent upon the price charged for brimstone and that the fixing of that price was in the hands of those who controlled the Sicilian industry. This having been duly recognised in Great Britain, attempts were made to employ pyrites as the source of sulphur instead of brimstone, and in 1813 a patent was granted to Hill, of Deptford, in connection with this application. But Sicily continued to hold the sulphuric acid raw material trade until the year 1838, when a monopoly was granted by the King of Naples for the export of Sicilian sulphur to M. M. Taix & Cie., of Marseilles. The result of this monopoly grant was to raise the price of brimstone from £5 to about £14 per ton. The immediate answer of Great Britain was that much work was done and many patents were taken out in connection with the application of pyrites to the manufacture of sulphuric acid, and shortly afterwards a large industrial plant was successfully installed by Thomas Farmer of London. As a result, brimstone was speedily replaced by pyrites, and Sicily lost nearly the whole of this trade. A certain proportion of the world's supply of sulphuric acid is, however, still made from brimstone, owing to the fact that brimstone made acid is free from arsenic, and as such is suitable for the preparation of sulphuric acid used in the preparation of products connected with food and pharmacy. Notwithstanding that the arsenic can be efficiently removed from sulphuric acid made from pyrites, brimstone is still preferably employed in this connection.

In order to meet the competition occasioned by the successful application of the Frasch process to the winning of sulphur in Louisiana, Professor G. Oddo proposed the employment of 'smalls' (*sterro*), which constitute about 20 p.c. of the Sicilian sulphur ore, for the production of sulphuric acid by means of the Herreshoff furnace. A large-scale plant was erected and worked, and it is claimed that successful results were achieved. Owing, however, to the very small percentage of sulphur contained in the 'smalls,' as compared with that contained in pyrites employed in industry, it was found that the cost of carriage would render the export of *sterro* to other countries impossible, and that the only chance of success was to start a sulphuric acid industry upon a very large scale in Sicily. This, however, has not yet been attempted.

The industry was not only damaged as regards the sulphuric acid industry by the rise in price of sulphur to £14 per ton as abovementioned, but as might have been expected, great harm was done in other directions. As a result, the monopoly was in due course withdrawn and the price of £5 per ton re-established. Excepting the use of sulphur in the manufacture of sulphuric acid, all went smoothly as regards the world's supply until the Chance-Claus process for the recovery of sulphur from alkali waste became a success. From about 1891 to 1896, it was stated and believed that this process could not only be applied to the waste then being produced in the alkali industry, but also to the recovery of sulphur from the waste upon tip heaps which had been accumulating for many years past. Had this been possible, the vast quantity of sulphur recoverable would undoubtedly have revolutionised the sulphur industry of the world. Advantage was taken of the possibility to cause internal competition amongst the producers in Sicily, with the result that the market was completely disorganised and wages were reduced almost to starvation rates. This depression of prices reacted in turn upon the price of the Chance-Claus sulphur produced in England. In due course it was ascertained that it was not possible to extract the sulphur from the tip heaps waste, owing to the change it had undergone through oxidation, and it being known that the amount produced from fresh waste would not exceed 50,000 tons per annum, and therefore could not affect the Sicilian market, the price was fixed by speculators at about £5 10*s.* per ton. This action was resented by the consumers, who took the necessary steps to start a keen fight, not only between the producers in Sicily but also in Great Britain, with the result that the selling price of brimstone was reduced to 45*s.* per ton, out of which had to be paid the export tax of 8*s.* per ton. This state of affairs continued for some time, until 1896, when Sicily was on the verge of revolution as well as ruin.

It was then that efforts, initiated in England, were made to combine the Sicilian and British interests and to regulate the trade of the world, so that the price could no longer be dictated by speculators. At the same time, steps were taken to remedy the serious grievances of the Sicilian workmen and owners of mines. The movement, which resulted in the formation of the Anglo-Sicilian Sulphur Company, was heartily supported by the Italian Government and notably by the Marquis di Rudini, then Prime

Minister in Italy, with the result that the capital for the organisation of the business having been obtained mainly in England, a Royal Decree was then issued, and subsequently confirmed by a special Act of Parliament by which the heavy export tax was abolished, wages of the workmen increased, child labour, previously employed to a very large extent, was abolished, income tax and other heavy charges were withdrawn, and a tax of one lire per ton on sulphur exported was substituted. The bulk of the stock both in Sicily and England was taken over at an agreed and reasonable price, and an agreement was also made whereby about 65*s.* per ton would be paid to the producer in Sicily, and the production should be regulated so as to keep in touch with the quantity exported. The capital of the company was one million sterling, of which £735,000 was fully subscribed.

The formation of this company resulted in the maintenance of fair and satisfactory prices for sulphur, and of peace and prosperity for Sicily for a period of about ten years. Both buyers and sellers were satisfied with the conditions under which the company's business was carried on, and the variations of selling price during the ten years did not amount to more than 5*s.* per ton.

The contracts which the company made with the producers and the stock of sulphur which it acquired when it was formed gave it a control over about 75 p.c. of the total production of Sicily, and this led to the complete control of the market. The company also had the right under its contracts to call for a reduction of 18 p.c. of the output in any year in which the output should exceed the sale. But the producers were also entitled to be paid 1 p.c. extra for each 3 p.c. reduction in the price of sale. The company was only interested in the sale of sulphur and was in no way financially interested in the mining or in the process of production. It may be stated that the operations of the company were quite successful to all interested, and it would undoubtedly have continued to exist and to prosper but for the unexpected competition caused by the successful development of the Frasch process. It succeeded in obtaining a fair but not excessive market price for sulphur all over the world. For instance, in May, 1896, just previous to the formation of the company, the price of 'seconds' in New York was about 63*s.* per ton. In October of the same year, after the company had started operations, the selling price of the same quality was 104*s.* per ton.

The stock acquired by the company was about 60,000 tons, which, as representing about 70 p.c. of the industry of Sicily, was to be regarded as quite a satisfactory quantity. During the first eight years of the company's existence, no complications of any kind were experienced, but during the year 1904, the Frasch process was proved to be an industrial success, and the United States sulphur sales were from that time gradually taken away from the Anglo-Sicilian Sulphur Company. As a result, the company in July, 1906, exercised its option of terminating its agreement with the producers and was in due course liquidated with results which were completely satisfactory to the shareholders. The effect of competition with Louisiana sulphur will be appreciated when it is stated that the stock of the Anglo-Sicilian Sulphur Company, when it terminated its contracts, amounted to no less than 360,000 tons, and at the end of June, 1912, the stock of sulphur in Sicily amounted to no less than 546,902 tons. This had been reduced by the end of January, 1913, by limiting production, to 441,775 tons.

The Italian Government found it necessary again to support the sulphur industry when the Anglo-Sicilian Company was about to be liquidated, and with its assistance the stock of the company, amounting to 360,000 tons, was purchased at 49*s.* 2*d.* per ton, and was paid in Government debentures yielding 3·65 p.c. interest per annum redeemable in twelve years. The industry was placed, as from the 1st August, 1906, under the direction of the 'Consorzio obligatorio per l'Industria Solfifera Siciliana,' which was charged with the sale and regulation of the production of Sicilian sulphur for a period of twelve years. The Consorzio was assisted by the Government so as to be provided with sufficient capital to permit of its paying four-fifths of the selling value in advance to the producer for delivered crude sulphur, and also had full power to limit production. Sulphur was exempted from all taxation.

Considering the difficulties that have had to be faced as a result of the displacement of Sicilian output by Frasch sulphur, it may be stated that the Consorzio has constituted a successful organisation. Some modifications of the law relating to it were passed in Parliament in the years 1907, 1908, and 1909, by means of which the number of directors was reduced and full powers were given to restrict the output from the mines to the quantity sold for export. The result has been a very great reduction in the stocks now held in Sicily as above mentioned.

Louisiana sulphur. The deposits from which this sulphur is obtained are geologically associated with 'Dome Formations,' which constitute a striking feature of the coastal plains which extend through the States of Louisiana and Texas and the Gulf States of Mexico. Petroleum and rock salt of remarkable purity (98–99 p.c.) are also found in these formations in abundant quantity. The oil was first exploited, and it was when oil drilling was being carried out by the Louisiana Oil Company, in the year 1865, at the head of Bayou Choupique, about fifteen miles west of Lake Charles, that the first sulphur bed was found at a depth of 443 ft. It was proved that this sulphur bed had a depth of about 100 ft. Further detailed examination showed that the sulphur deposits have an average overburden of about 464 ft., consisting of about 376 ft. of clay and sands (pleistocene), quicksand and gravels (Port Hudson and Orange sand groups), and about 88 ft. of soft rock, mainly grey limestone. The average depth of the sulphur bed is 125 ft. Beneath the sulphur is gypsum with occasional layers of sulphur.

Between the years 1868 and 1895 many attempts were made to win the sulphur by ordinary shaft mining and by modifications of the same. They all resulted in hopeless failure, loss of many lives and great loss of capital. Among the companies formed for the purpose of mining the sulphur may be mentioned the

Calcasieu Sulphur and Mining Company, the Louisiana Sulphur Mining Company, the American Sulphur Company, a French company which spent £300,000 upon a scheme for the employment of machinery specially devised for overcoming the difficulties, and an Austrian company. These difficulties were mainly twofold: to resist the lateral pressure upon the shaft due to the enormous amount of moving water contained in the quicksands, and to prevent the inrush of the sand waters into the sulphur bed, when it had been penetrated, owing to the fact that there was no roof over the sulphur bed. These waters were found to be permeated with sulphuretted hydrogen and sulphurous acid gas which proved fatal to the miners. In 1893, E. P. Rothwell, acting as manager to a New York company, sought to overcome the difficulty by lining the shaft with two cast-iron tubes cemented together. The lateral pressure was thus withstood and the sulphur bed was reached, but the inrush of gases again proved fatal to the workmen and the scheme had to be abandoned.

It will be seen that during no less than thirty years, successive attempts were made to win sulphur from what were proved by borings to be vast deposits, but ordinary mining operations were found to be absolutely impracticable.

The Frasch process. This may fairly be described as one of the triumphs of modern technology, and the result of its successful development has been to provide a great industry for the United States, which it did not previously possess, and to remove from Sicily to that country the domination of the conditions regulating the world's supply of sulphur.

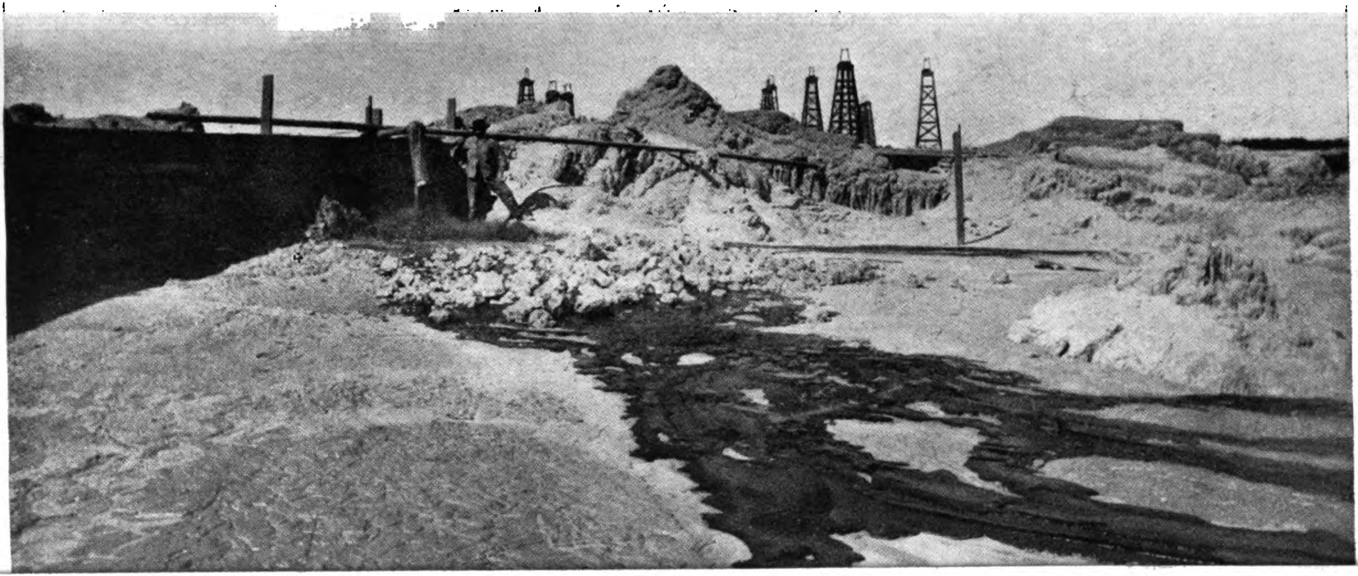
Herman Frasch, who had long been engaged in industrial research work in the United States in connection with petroleum drilling and refining, heard in 1891 of the difficulties connected with the mining of Louisiana sulphur, as above described. As a result of prolonged study, he arrived at the conclusion that the ordinary mining methods were inapplicable, but that the problem could be solved provided he could introduce superheated water into the sulphur bed through a tube passing through the quicksands at a temperature at or above the melting-point of sulphur and then raise the molten sulphur through another tube to the surface. The molten sulphur would then solidify on cooling at the surface, and the sulphur thus obtained would necessarily be of high purity. To succeed with this scheme meant not only to overcome the difficulties in connection with lateral pressure upon the tubes already alluded to, not only to introduce the superheated water to the sulphur about 500 ft. below the surface at the required temperature, but, recognising that a pool or well of melted sulphur would be formed below the bottom of the tube by this superheated water, it would be necessary to raise this molten sulphur from the pool or well to the surface before it could be cooled below melting-point by the incoming water from the quicksands.

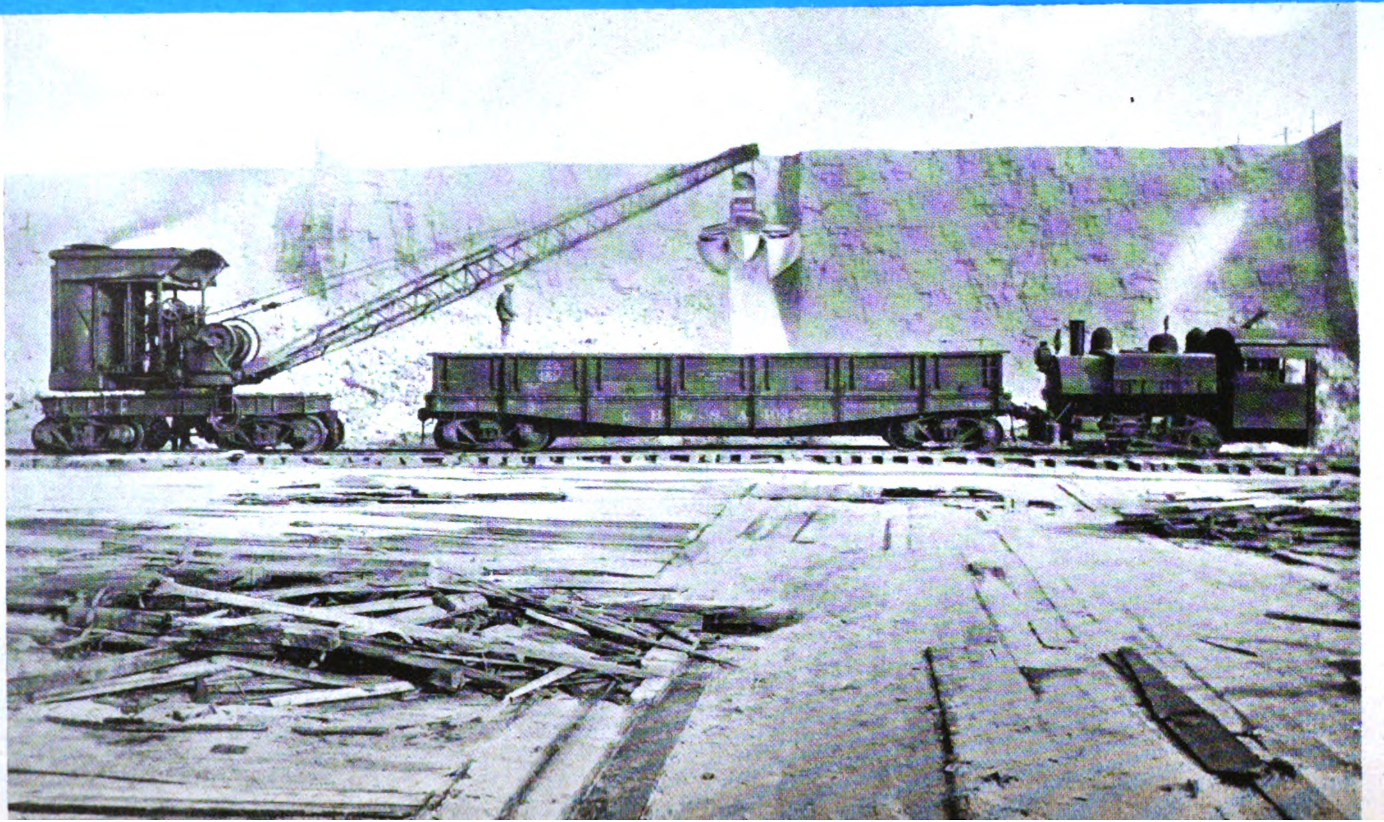
He and his associates purchased land within a short distance of the sulphur mine then being worked by the New York Company. He drilled four wells to a depth of 2000 ft. each and found no sulphur. He concluded that the New York company's property was located where the sulphur was concentrated in bulk, and in conjunction with his associates he acquired this property in the name of the Union Sulphur Company of Cleveland, Ohio. It consisted of a flat lying area of 5000 acres, situated near the parish of Calcasieu, Louisiana, 80 miles from Port Arthur, Texas, on the Gulf of Mexico, and 228 miles from New Orleans. The property is about 50 miles east of the great Texas oil field at Beaumont and is geologically the eastern extension of that field. As a result of many trial drills it is estimated that the Louisiana deposits contain not less than 40 million tons of sulphur, and that it would be a conservative estimate to conclude that not less than half this quantity can be brought to the surface by the Frasch process.

As may be imagined, many difficulties were encountered in working out the process, and it was not until the year 1903, when 35,000 tons of sulphur were brought to the surface, that success may be said to have been achieved. The chief trouble arose in connection with the pumping up of the molten sulphur, mainly due to the breaking down of the valves owing to corrosion. Zinc and aluminium valves were respectively tried, but were found incapable of standing the strain. Ultimately, pumping was replaced by an 'air lift,' by means of which the molten sulphur is forced through a tube to the surface. An additional advantage resulting from the use of the compressed air is that the specific gravity of the mixture of air and sulphur which is raised is lower than that of molten sulphur by itself, and hence the strain upon the great length of piping is reduced. The mixture employed is two parts by volume of air to one part of molten sulphur.

The following may be regarded as a substantial description of the process as worked: A well, 17 ins. in diameter, is bored to a depth of some 50 ft. This is not provided with a casing, but a mixture of clay and water is pumped down with a view to fill up the interstices in the sand, whereby caving is greatly reduced. Within this well a wrought-iron pipe, 13 ins. in diameter, is sunk to a variable depth, dependent upon outside pressure, and sometimes it can be arranged to reach the bottom of the quicksands at about 250 ft. A mixture of clay and water is also employed in connection with this pipe, and in addition to helping to support the walls it materially facilitates the withdrawal of the pipe when the well is exhausted, thereby effecting a considerable economy in the working of the process.

Inside this 13-inch diameter pipe, an 8-inch diameter pipe is driven to the bottom of the sulphur bed. Water and clay are also used. Those sections of this pipe which are intended to be in the sulphur bed are perforated with holes of half an inch diameter, arranged in spiral form, the holes being six inches apart. This arrangement has for its object to prevent gypsum, &c., getting to the bottom of the pipe. The superheated water, which is conveyed through this pipe to the sulphur bed, has free access to the sulphur throughout the entire thickness of the deposit, and any substance which should by chance get into the bottom of the pipe causes no trouble. Inside the 8-inch diameter pipe, an unperforated 6-inch diameter





pipe is sunk to the bottom of the sulphur bed. Superheated water is also pumped down this pipe. Enclosed in this 6-inch pipe is an unperforated 3-inch diameter pipe, through which the molten sulphur is raised to the surface. Inside this 3-inch pipe is driven to the bottom of the bed a 1-inch diameter unperforated pipe through which the compressed air is forced.

Superheated water is pumped down the 8-inch and 6-inch pipes. The water from the 8-inch pipe melts the sulphur which (sp.gr. 2·06) sinks down alongside the pipe to the bottom of the sulphur bed. The water in the 6-inch pipe mainly serves to keep the sulphur hot in the enclosed 3-inch pipe, thereby preventing crystallisation on its way to the surface. Compressed air, at a pressure of 250 lbs. per square inch, is forced down the 1-inch pipe to raise the sulphur by the 'air lift.' This pressure is found sufficient in practice to raise the sulphur to the surface, as the air is helped by the head of water in the 6-inch and 8-inch pipes to overcome the weight of sulphur in the 3-inch pipe.

One of the most important features of the process—indeed, that upon which successful working mainly depends—is the maintenance of a proper adjustment between the pressure of the superheated water and the air pressure so as to allow of the uninterrupted flow of sulphur through the 3-inch pipe. If the air pressure be too great, the liquid sulphur is kept away from the 3-inch pipe and superheated water gains entrance to it. When the water and the molten sulphur come into contact, the sulphur granulates, subsequently causing clogging in its upward path. As a result there is irregular discharge of the sulphur, and this means such great local pressure in the pipe that serious breakage is apt to occur. It has been found advisable, in this connection, to so adjust the respective lengths of the pipes that the 8-inch and 6-inch pipes are a few inches shorter than the 3-inch and 1-inch pipes as they stand in the well. What is aimed at is to have a constant pool of sulphur surrounding the bottom of the 3-inch pipe.

It has been found advisable to introduce sawdust with the superheated water once the pool of liquid sulphur has been formed. It is found that this prevents to a very great extent the flow of quicksand water into the pool with consequent lowering of temperature. When the well is exhausted, before the withdrawal of the 8-inch pipe, it is now usual to replace with earth the space of the extracted sulphur and thus prevent subsequent subsidence of the earth as much as possible. In order to obtain the sandy earth necessary for this purpose, the Union Sulphur Company have provided a dredging plant in the vicinity of their works with a capacity of 4000 cubic yards per day. Notwithstanding this precaution, considerable subsidence is stated to have taken place.

It is obvious that in working this process so as to produce a yield of, say, 250,000 tons of sulphur per annum, an enormous supply of water is necessary. It is stated that the average daily consumption is about 7,000,000 gallons. To provide for this, the Union Sulphur Company have constructed a pumping station on a river about six miles from the works, to which the water is conveyed by means of a canal; as a standby there is also provided at the works a reservoir covering 150 acres.

To supply the necessary heat and power, the latter constituting only a fractional percentage, it is found that each well requires a battery of 15 or 20 boilers of 50 h.p. each. Steam pressure runs at about 100 lbs. The total boiler capacity at present installed is stated to be about 25,000 h.p. Crude oil is used as fuel and its local availability and cheapness have undoubtedly largely contributed to the successful working of the Frasch process. There are two oil burners to each boiler. It is stated that the present daily consumption of crude oil is about 700 barrels at each battery, and that the average annual consumption is upwards of 1,000,000 barrels.

The boilers supply steam to six heaters, each 15 ft. high and 3 ft. in diameter. Two direct acting horizontal pumps, working under a stroke of 38 to 40 per minute, supply each heater with the necessary water at a temperature of 140°F. (C. = 60°). The steam enters the heaters at the top and the water at the bottom, and the superheated water leaves the heater at a temperature varying from 340°F. (C. = 171·1°) to 360°F. (C. = 182·2°) under an absolute pressure of 104 lbs. to 140 lbs. The water is conducted to the well by means of insulated pipes. The melting-point of sulphur is 239°F. (C. = 115°), and at a temperature slightly below this it will granulate.

It has been estimated that of the total heat units employed, 0·5 p.c. only are utilised in melting the sulphur. The temperature of the quicksand water, of which there is a great influx to the sulphur bed during the operation of the process, is low and has to be raised before the sulphur can be melted. The well gives out when the cavity from which the sulphur has been extracted becomes too large to permit of the necessary temperature being maintained.

Each well is driven by the ordinary oil-well driller mounted on a derrick from 75 ft. to 100 ft. high; five men generally constitute the drill gang. The average time required for drilling the well may be said to be between three and four weeks. The speed of drilling naturally varies with the nature of the material to be passed through, but it is stated to average 80 ft. per day through the quicksand, from 5 ft. to 8 ft. per day through the limestone rock, and 20 ft. to 30 ft. per day through the sulphur.

The average cost of sinking each well, exclusive of pipes, is stated to be about £400, and the expense of working the well during its life, including oil, labour, depreciation, &c., will average about £2000 more. The wells are sunk in groups, the wells being placed from 50 to 100 ft. apart. The output from a well is obviously liable to considerable variation. It is stated that as much as 73,000 tons of sulphur were obtained from one well. This is undoubtedly exceptional, but a good idea of the output may be obtained from the statement that as much as between 400 tons and 500 tons have been produced per well per day during some months. The total annual production is restricted to meet the world's demand, in conjunction with other sources of supply, but the average is now not less than 250,000 tons per annum.

On reaching the surface the sulphur is

conducted through a pipe supported on a light framework to a bin roughly constructed of beams in which it quickly solidifies. At the early stages of working these bins were divided into compartments into which the sulphur was allowed to flow until it had acquired a depth of 9 ins., when the flow was diverted to another compartment, so as to permit of the cooling of the collected 9 ins. After solidification, another 9 ins. of sulphur was allowed to flow in, and the bin was by this method finally filled up. The bins as now used are about 150 ft. by 250 ft. and about 65 ft. high. The sulphur is delivered into the centre of these bins and caused to spread in layers about 1 in. thick. By this method of working, the cooling is sufficiently rapid to permit of continuous operation. As much as 150,000 tons of sulphur have thus been accumulated in one series of bins.

From 600 to 700 men are employed in winning and despatching the sulphur, and, having regard to the quantity dealt with, this is a notable proof of the up-to-date character of the labour-saving methods adopted. A comparison of these figures with the labour employed for the Sicilian output is vastly in favour of the Frasch process. Further, if the total cost of obtaining the sulphur be considered, it is obvious that commercial competition by Sicily with Louisiana would be impossible, but the supply of the world's consumption from the respective sulphur-producing countries is now said to be regulated by arrangement, so that Sicilian sulphur is able to realise a reasonable profit.

In order to remove the sulphur from the bins to the railway trucks, the wooden hoarding is removed and blasting applied to the bottom of the sulphur. In this way the sulphur on being shot down by the blasting is so broken up that it can be picked up by grab buckets, which, by means of cranes, discharge it into wagons at such a speed that a 35-ton wagon can be filled in about 14 minutes. It is stated that as much as 1000 tons per day have thus been loaded for periods of 20 to 30 consecutive days.

For some considerable time after the process was started, the sulphur was conveyed by rail to New Orleans, about 228 miles distant. This was superseded by the construction of a special line, 68 miles in length, to Port Sabine, Texas. The cost of transport to New York has, in this way, been reduced to about one-third of what it previously was. The loading on to ships at Sabine is effected by mechanical arrangements, thereby reducing the cost to one-tenth of what it used to be at New Orleans, and it is stated that the sulphur can be evenly loaded on to the ships at the rate of 600 to 800 tons per hour. The company owns ships specially constructed for sulphur transport, and one of them will carry 5500 tons.

The stocks of Louisiana sulphur in the United States, France, and Hamburg may be said to amount to fully 400,000 tons.

The sulphur obtained by the Frasch process is of a very high degree of purity, from 99·93 p.c. to 99·98 p.c., and in addition only contains a trace of water. The process is only applicable when the deposit is especially rich in sulphur—say, between 60 p.c. and 70 p.c.—and for this reason, amongst others, it is not available for use in Sicily.

Up to the present, the Louisiana deposit owned by the Union Sulphur Company practically supplies all the sulphur obtained in the United States. Endeavours have been made, and are still being made, to locate other deposits in the same geological formations and to organise their development.

In recognition of the work involved in devising and industrially working out this process, Herman Frasch was, in December, 1911, awarded the Perkin medal of the Society of Chemical Industry.

Geological Survey of Louisiana, 2 vols., 1899 and 1902, U.S.A. Geological Survey; Zeitschrift Deut. Geol. Gesellschaft (Preussner), 1888, vol. xl. p. 194; Oil Fields of the Texas-Louisiana Gulf Coastal Plain, U.S.A. Geological Survey, Series A, Economic Geology, Bulletin No. 212, 1903; Mineral Industry, vols. 1 to date; The Journal of Industrial and Engineering Chemistry, Feb. 1912, pp. 132 *et seq.*, published by the American Chemical Society, containing—Geology of the Sulphur and Sulphur Oil Deposits of the Coastal Plain, by A. F. Lucas, p. 140; Sulphur Mines of the Union Sulphur Company in Louisiana, by F. H. Pough, p. 143.

From alkali waste. The recovery of sulphur, as such, from the calcium sulphide contained in alkali waste, a by-product of the Leblanc process, and the conversion of the calcium, with which it was previously combined, into an industrially available product, was taken in hand by several recognised leaders of the alkali industry. But it required about fifty years of almost continuous work before commercial success was achieved.

In 1837 Gossage devised a process at the development of which he worked for many years. It was based upon the decomposition of the calcium sulphide by means of carbon dioxide obtained from lime-kiln working, and the subsequent recovery of the sulphur from the sulphuretted hydrogen gas thereby generated. But although his labours undoubtedly contributed largely to the ultimate solution of the problem, he was unable himself economically to produce either sulphur or sulphuric acid, due to his failing to overcome the difficulties connected with the state of extreme dilution, and also the very variable strength of the sulphuretted hydrogen generated.

Ludwig Mond in England and Mactear in Scotland worked upon similar lines, but their respective processes, though ingenious and theoretically sound, also failed to produce commercially applicable results.

Schäffner and Helbig (Eng. Pat. March, 1878) worked out a process at Aussig in Saxon Switzerland, based upon the following operations:—

1. The decomposition of alkali waste by heating it with a solution of magnesium chloride

$$CaS+MgCl_2+2H_2O=CaCl_2+Mg(OH)_2+H_2S$$

The magnesium hydroxide thus produced was found to be held in suspension by the calcium chloride.

2. Magnesium chloride was reformed by acting upon the suspended magnesium hydroxide with carbon dioxide, and the calcium chloride converted into carbonate of lime available for industrial use

$$CaCl_2+Mg(OH)_2+CO_2=MgCl_2+CaCO_3+H_2O$$

It was subsequently found by Frederick Chance that in this reaction, the average loss of magnesium choride (calculated as magnesium) amounted to 1·05 parts per 100 parts of alkali waste operated upon.

3. The sulphuretted hydrogen gas liberated was treated for sulphur production with a view to effect the reaction

$$2H_2S+SO_2=2H_2O+3S$$

This had been previously attempted, but no satisfactory yield could be obtained owing to the formation of thionic acids (Debus, Chem. Soc. Trans. 53, 278).

This formation Schäffner and Helbig endeavoured to prevent by causing the gases to react in the presence of a definite quantity of calcium chloride or magnesium chloride. By their process the necessary sulphur dioxide was obtained by burning one-third of the H_2S into SO_2 and steam, and this mixture was passed, together with the remaining two-thirds of the H_2S, up a tower filled with blocks of wood over and down which a solution of calcium chloride was caused continuously to trickle. The latter on issuing from the tower contained the free sulphur in suspension and it was subsequently recovered.

This process, although a great improvement upon what had previously been achieved, did not entirely prevent the formation of thionic acids. Indeed, it was stated by Weldon that such formation amounted to nearly 10 p.c. of the total sulphur present, and that the maximum yield of free sulphur amounted to a very little over 80 p.c.

The process was taken in hand by A. M. Chance and his colleagues at their works at Oldbury and two years of experimental trials were devoted to it. As a result, it was proved that the production of sulphur, as such, by this process, did not constitute a commercial proposition owing to low yield, &c., but it was also proved that by burning all the sulphuretted hydrogen gas into sulphur dioxide it was possible to produce sulphuric acid at a price corresponding to 3*d*. per unit of sulphur per ton of Spanish pyrites, whereas the price had been previously maintained at 6*d*. per unit. The process was industrially worked for some little time, but had to be stopped when the Tharsis Company reduced their price of pyrites to 3*d*. per unit and made contracts with alkali makers at this price extending over a period of years.

Undaunted by this reverse, Chance continued his work, and with the able assistance of H. W. Crowther and others he succeeded, four years later, in 1887, in producing sulphur at a price which permitted of competition with Sicilian brimstone. There can be no doubt that the adoption of this process by the Leblanc alkali makers was very largely responsible for their being able to continue the Leblanc as opposed to the Solvay ammonia soda process, and thereby avoid the scrapping of plant involving huge loss of capital. The process has been worked continuously since its introduction and is still employed by the Leblanc alkali makers. It is difficult to obtain accurate data as to the quantity of sulphur which has been thus produced, but from trustworthy information it may be stated that the minimum output has been about 35,000 tons per annum, mainly manufactured in Great Britain, and that therefore since the installation of the process it has yielded a minimum production of about 840,000 tons of sulphur.

The process, known as the Chance-Claus process, is based upon the lines followed by Gossage, of decomposing the calcium sulphide of vat waste by means of the carbon dioxide obtained from lime kilns and of recovering the sulphur from the sulphuretted hydrogen gas thus generated. But one of the essential features of success was to obtain both the carbon dioxide and the sulphuretted hydrogen gas in a state of concentration.

It had previously been found impossible to obtain lime-kiln gases containing more than an average of 30 p.c. of carbon dioxide, the remaining 70 p.c. consisting essentially of nitrogen. The presence of this latter obviously caused the dilution of the sulphuretted hydrogen and to such an extent that the economic production of sulphur was impossible. It was further found that the amount of sulphuretted hydrogen varied from 1 p.c. of the total gases up to not exceeding 35 p.c.

Chance succeeded in obtaining a constant yield of sulphuretted hydrogen of very high strength (Eng. Pat. 8666, 1887). This was effected by employing a series of communicating vessels provided with inlet and outlet mains. The vessels contained the alkali waste mixed with water in the form of cream to which a given proportion of caustic lime was, if necessary, added. The lime kiln gases, on being passed into the first vessel of the series, give up the carbon dioxide to the free lime present, forming calcium carbonate, and the sulphuretted hydrogen together with the nitrogen is passed on into the next vessel of the series. The sulphuretted hydrogen is then absorbed, calcium hydrosulphide (CaH_2S_2) being formed. This process of absorption is continued throughout the series, and as finally worked out acts so efficiently that the gas issuing from the last vessel contains only traces of sulphuretted hydrogen and carbon dioxide, the former being recovered by passing through bog oxide or lime and the nitrogen allowed to escape into the air. The inlet and outlet mains are so devised that the respective vessels can be arranged in any order to constitute the series. In due course the carbon dioxide acts upon the calcium hydrosulphide formed as above described

$$CO_2+CaH_2S_2+H_2O=CaCO_3+2H_2S$$

The gas thus generated is mixed with sulphuretted hydrogen issuing from another vessel, and by suitable regulation of the vessels high strength of gas is obtained. The sulphuretted hydrogen is then conducted to a gas holder of about 30,000 cubic ft. capacity, escape of gas being prevented by the use of 'dead oil.' In practical working it has been found that the sulphuretted hydrogen thus conveyed to the gas holders contains about 2 p.c. of carbon dioxide. So long as there is no condensation of moisture on the plates of the gas holder, this amount of carbon dioxide will do no harm, but in presence of moisture the corrosion of the gas holder plates may become a serious matter. To ensure the absence of such moisture the gas holders should be placed a few hundred yards from the series of vessels, which are termed carbonators. The gas is conveyed to the holders through a 12-inch main and when leaving the carbonator it is distinctly warm; but by passing through say 300 yards of this main the gas is found to be cooled practically to atmospheric temperature before it enters the holder, and thus condensation in the holder itself is prevented. This precaution has been found to prolong the life of the holder very greatly and thereby to exercise a very important effect upon the economical working of the process.

The yield of sulphur obtained as sulphuretted hydrogen by this process may be taken as not less than 90 p.c. of the total sulphur contained in the vat waste.

Vat waste contains salts of soda, and when the decomposition as above described is completed these are found to be converted by the action of the carbon dioxide into sodium bicarbonate. This is ultimately recovered, because the mud which contains it is used for black ash making instead of chalk. In this way about 3 p.c. of soda calculated upon the alkali produced, which by the old method of working was lost, is recovered.

The concentrated sulphuretted hydrogen thus obtained is next treated with a view to the recovery of the contained sulphur by a process invented by C. F. Claus (Eng. Pats. 3608, 1882; 5070, 5958, 5959, 5960, 1883). This was originally devised for the recovery of sulphur from the sulphuretted hydrogen contained in coal gas, but it was recognised by Chance that it could be made applicable to the solution of one important part of the problem at which he was working. He therefore acquired the patent rights, and after four years' work at Oldbury, largely devoted to securing a continuous exact supply of the necessary quantity of air to decompose the sulphuretted hydrogen, success was achieved.

Anhydrous ferric oxide is used for the absorption of the sulphuretted hydrogen. This oxide is placed upon a bed within the kiln, which bed consists of broken fire brick or other suitable chemically inert material. It is maintained at a temperature which keeps the ferric oxide at a dull red heat. This temperature results from the heat of the reaction, but it may if necessary be supplemented. The sulphuretted hydrogen mixed with the necessary quantity of air to bring about the formation of sulphur and steam is passed through the anhydrous ferric oxide: the volatilised sulphur together with steam pass out of the kiln into chambers where the sulphur is deposited. It may be obtained either as fused or sublimed sulphur, dependent upon the temperature of the kiln and of the depositing chambers. The ferric oxide undergoes no change and may be continuously used. The sulphur obtained by this process is of a high degree of purity.

See Journal Society of Chemical Industry, 1881, vol. 1, p. 45; Journal Society of Arts, 1882, p. 724; Journal Society Chemical Industry, 1882, vol. 1, p. 264; Journal Society Chemical Industry, 1883, vol. 2, p. 10; Journal Society Chemical Industry, 1883, vol. 2, p. 202; Journal Society Chemical Industry, 1884, vol. 3, p. 392; Journal Society Chemical Industry, 1888, vol. 7, p. 162. See also SODIUM, p. 54 *et seq.*

Uses of sulphur. Notwithstanding that the use of sulphur has practically become negligible in connection with the preparation of black gunpowder, and also that as it has, except to a very limited extent, been replaced by pyrites in the manufacture of sulphuric acid—the two industries which at one time accounted for the major portion of the consumption—there has nevertheless been a great increase in the world's annual requirements.

This is largely accounted for by the enormous development in the manufacture of paper from wood, due principally to the work of Ekman, Kellner and Partington. It is estimated that upwards of 180,000 tons of sulphur are yearly used in this connection, and that about 280 pounds of sulphur are required for every ton of wood pulp produced. The sulphur is used for the manufacture of calcium bisulphite and magnesium, but more particularly the former. The bisulphite thus manufactured is added to the wood chips in a very dilute solution: indeed 5 p.c. of total SO_2 may be regarded as the maximum, and of this about 2 p.c. is purposely uncombined. It is essential that not more than traces of sulphuric acid be present, otherwise the pulp is injuriously affected. These two facts account for sulphur not having been replaced by pyrites in the manufacture of wood pulp bisulphites, because the dilute solution employed makes it practically necessary to manufacture the bisulphite where the wood pulp is made. The cost of transport per unit of sulphur available for conversion into sulphur dioxide is therefore a serious consideration. Moreover, it has not been found practicable to sufficiently limit the quantity of sulphuric acid present if the sulphurous acid is made from pyrites.

Sulphur is used to the extent of upwards of 100,000 tons per annum in Europe alone for preventing the growth upon the shoots and grapes of vines of the microscopic mould fungus *oidium*, which if allowed to develop causes the vine leaves to dry up: as a result, the grapes, when ripe, produce an unsound wine. The sulphur employed for this purpose is largely in the form of flowers of sulphur, although winnowed sulphur prepared as already described is also used.

The efficiency of sulphur as a preventive of the growth of *oidium* is considered to be largely dependent upon its physical condition. Thus, flowers of sulphur contain a certain proportion of amorphous sulphur which is much more easily oxidised than the crystals, even when in a very fine state of division. It is believed that by air exposure minute quantities of sulphurous acid and sulphuric acid are formed, which by their presence cause the destruction of the *oidium*. The question of the autoxidation of sulphur has been investigated by Windisch, August Harph (Zeitsch. anorg. Chem. 1904, 39, 387–388) and others, and from their work the conclusion as to the cause of destruction of the *oidium* would appear to be justified. In connection with the use of sulphur in viticulture, it should be pointed out that a very large quantity is used in addition to that mentioned above in the form of what is known as 'Bouillie Bordelaise,' which consists of a mixture of sulphur, copper sulphate, and various porous substances. This mixture is applied to the shoots and grapes of the vines.

Sulphur is also effectively used to prevent the growth of mould on hops. If the growth is not prevented the hops are practically useless. The mould in question is also an *oidium*, the species being similar to that found upon the vine. The fungus grows upon the upper and lower surfaces of the hop leaves, and if allowed to develop forms a white powdery spot on the 'burr' or buds of the hop cones. This stops the development of the cone into the hop, and hard, white knobs are formed which later on turn black. This black colour is due to mould, but when the hops get ripe a further variation in colour is apt to appear, known as 'red mould.' Flowers of sulphur are used as a preventive of hop mould. The total quantity used will vary from season to season, but on the average it is considerable.

Sulphur is also always burnt in the oast houses when the ripe hop-cones are being dried. For this purpose, 'rolled brimstone' is employed. The sulphur is burnt underneath the hops and fumes of sulphur dioxide are passed through the hops. The amount of sulphur thus employed averages about half a pound of sulphur per 10 bushels of green hops. The effect of the passing of sulphur dioxide through the hops is to bleach them, to improve their flavour, and to hasten the drying process (Amos, J. Inst. Brewing, 1910, 16, 142).

Sulphur is used upon a very considerable scale for the manufacture of bisulphite, mainly of calcium, employed as a preservative for fermented beverages, notably ale. It is also used for making sulphurous acid, which is employed to remove the smell of sulphuretted hydrogen which is liable to accumulate in wine barrels, and also to act as a disinfectant.

Sulphur is used in these cases because of its freedom from arsenic. The same remark applies to its application to the manufacture of sulphuric acid when the latter is required for the preparation of foodstuffs or pharmaceutical products. Sulphur is used in the treatment of cutaneous diseases, mostly in the form of ointments. It is also employed medicinally under the name of *milk of sulphur*, which is a precipitated amorphous powder prepared by precipitating the sulphur from a solution of calcium sulphide and thiosulphate by means of hydrochloric acid. Its medicinal properties are stated to be similar to those of sublimed sulphur only more active. Milk of sulphur should be completely soluble in carbon disulphide.

It has already been pointed out that one reason for employing sulphur instead of pyrites in the manufacture of bisulphite for wood pulp treatment is due to the great economy in transport per unit of available sulphur. The same argument holds good in connection with the manufacture of sulphuric acid employed in the making of high explosives for blasting purposes in South Africa, where sulphur is now used. A little more than 40 p.c. of sulphur is available for the production of sulphur dioxide calculated upon the weight of the pyrites, whereas 98 p.c. of available sulphur is derivable from brimstone.

Recent experiments indicate that flowers of sulphur will, in many cases, act as an efficient fertiliser. The addition of small quantities (0·023 grm. per kilo) to the soil was found to materially assist the growth of carrots, beans, celery, lettuce, sorrel, endive, potatos, onions, and spinach, the increase in the weight of the vegetables being, in some cases, as high as 40 p.c. and not lower than 10 p.c. It is suggested that the sulphur only acts indirectly by modifying the development of the soil bacteria. This view is based upon the fact that it was found useless when applied to sterilised soil. It is also asserted that sulphur exercises a favourable influence upon the development of chlorophyll, and plants grown upon a soil to which sulphur has been added are a much deeper green (E. Boullanger, Compt. rend. 1912, 154, 369–370, and A. Demolon, *ibid.* 1912, 154, 524–526).

The vulcanisation of rubber is effected by the addition under recognised conditions of sulphur to india rubber. Sulphur chloride, a solvent of sulphur, is used for vulcanising caoutchouc. The sulphur chloride of industry is a mixture of S_2Cl_2 and SCl_4.

Sulphur enters into the composition of certain cements. For this purpose, it is melted with iron filings and ammonium chloride; or, instead of melting the mixture, 100 parts of filings may be mixed with 5 to 15 parts of sulphur. To this mixture is added about 5 parts of ammonium chloride. The whole is then moistened with water and well mixed. Both mixtures yield cements useful for fixing glass to metal.

Sulphur is also used in the manufacture of carbon disulphide, artificially made sulphides, hyposulphites, in the bleaching of silk and wool by means of sulphur dioxide, in the manufacture of ultramarine, and of artificial vermilion, and in the making ot enamels.

Properties. Several allotropic varieties of sulphur are known, characterised by differences in crystalline form, specific gravity, behaviour towards solvents, &c. The two varieties known as α-sulphur and β-sulphur were first isolated by Mitscherlich (Pogg. Ann. 1825, 264).

α-Sulphur consists of rhombic octahedra which are obtained when sulphur is crystallised at normal temperatures or even at a temperature not exceeding 98°; also from solutions in carbon disulphide by evaporation in the cold. Fine crystals of this type are also obtained by oxidation in air of a solution of sulphuretted hydrogen in pyridine (Ahrens, Ber. 1890, 23, 2708). Natural sulphur as mined is always found in this crystalline form.

β-Sulphur belongs to the monoclinic system and is prismatic. It is formed when crystallisation is effected between 98° and 120°, this latter temperature being the fusion point of prismatic sulphur, as opposed to 114·5° for α-sulphur. β-Sulphur is also obtained from hot solutions of sulphur in alcohol, benzene and turpentine. Above 98° it is stable, but at normal temperatures it is slowly changed into the rhombic form. Heat is evolved as a result of the transformation, 2·27 cal. being liberated by the change of 32·07 grms. of the monoclinic into the rhombic form.

γ-Sulphur is obtained by slowly pouring molten sulphur into water. It is amorphous and to a certain extent elastic. It is insoluble in carbon disulphide, a property which, up to a varying proportion, is shared by flowers of sulphur. Indeed it has been suggested that the term flowers of sulphur should not be applied unless the sample, when newly made, contains not less than 33 p.c. of sulphur insoluble in carbon disulphide, and that if containing less than this it should be known as sublimed sulphur (A. Domergue, Ann. Chim. anal. 1904, 434).

When sulphur is melted at about 120°, it is very fluid, soft, and of a clear yellow colour, but if the temperature be raised to about 160° it becomes viscous and darker in colour: the maximum viscosity occurs at 180°. If the mass be cooled in water from this temperature, it is found that a portion is insoluble in carbon disulphide, but if the heating of the molten sulphur be continued and increased to near its boiling-point, the proportion insoluble in carbon disulphide greatly increases. At 250° sulphur is transformed into a blackish-red mass. At 444·5° (boiling-point) the sulphur has lost its viscosity and yields a reddish-brown vapour. Sulphur thus heated and subsequently cooled in water is known as *plastic sulphur*. If the insoluble sulphur thus obtained be kept for some time, it slowly reverts and is then soluble in carbon disulphide. Whilst at ordinary pressure molten sulphur yields prismatic crystals, under a pressure of 400 atmospheres it yields octahedral crystals (αS) without the necessity of superheating the molten sulphur (M. Lowry, Chemical World, September, 1912).

Amorphous sulphur is distinguished from γ-sulphur by being soluble in carbon disulphide. After several years keeping, it is found to change into α-sulphur. Milk of sulphur (*lac sulphuris*) or 'magister,' which is white, is another variety of amorphous sulphur. This, as stated already, is obtained by treating calcium pentasulphide (CaS_5) with dilute hydrochloric acid.

δ-Sulphur is obtained by passing sulphur dioxide into a saturated solution of sulphuretted hydrogen in glycerol (Sarazon, D. R. P. 216825), and is probably identical with the variety obtained by Debus (Chem. Soc. Trans. 1888, 53, 282) by passing sulphuretted hydrogen into an aqueous solution of sulphurous acid. This variety of sulphur is *colloidal*. According to Spring (Rec. trav. chim. 1906, 25, 253), it is a hydrate of sulphur S_8,H_2O. Colloidal sulphur can be obtained by a variety of methods (Engel, Compt. rend. 1891, 112, 866; Raffo, Zeits. Chem. Ind. Kolloide, 1908, 2, 358; Himmelbauer, *ibid*. 1909, 4, 307; Weimarn, J. Russ. Phys. Chem. Soc. 1910, 42, 481).

Nacreous sulphur (Gernez, Compt. rend. 1884, 98, 144, and M. Lowry, Chemical World, May, 1912) is also known as *mother-of-pearl sulphur*. It is produced by allowing a solution of sodium thiosulphate to diffuse into a solution of acid potassium sulphate. It may also be made by mixing and shaking hydrogen persulphide with ether, ethyl acetate or alcohol. Another method is by preparing a supersaturated solution of sulphur without residue when hot in benzene, toluene, carbon disulphide or alcohol. Place this in a tube and introduce the end of the tube only into a freezing mixture to which crystals of ammonium nitrate are added. Long nacreous flakes originate little by little at the cold point of the tube and gradually advance in the remainder of the liquid. The nacreous sulphur is formed in large colourless rhombic crystals.

Another variety of sulphur is prepared by submitting it to vaporisation in a transparent quartz vessel. By this means it is seen that, whereas the colour is at first deep reddish-yellow, this gradually disappears as the temperature is raised and the heating prolonged until it becomes practically colourless. It then acquires a pale blue colour, which remains until the vapour cools when the blue colour disappears. The same blue colour is observed when sulphur is volatilised in an atmosphere of carbon dioxide. Blue sulphur can also be prepared by heating it with soda. Black amorphous sulphur is thus obtained, and if this be thrown into fused borax or fused calcium chloride it acquires a very deep blue colour. It is also obtained by heating sodium thiocyanate (NaCNS) to 430° (N. A. Orloff, J. Russ. Phys. Chem. Soc. 1902. 34, 52; E. Paterno and A. Mazzucchelli, Atti. R. Acad. Lincei, 1907 [v.], 16, 1, 465).

An interesting variety of sulphur resembling india rubber, may be prepared by heating sulphur to above 400° and pouring it in a thin stream into liquid air. It is then obtained in the form of a thin thread of diameter 0·5 mm. to 1 mm. This thread, when first removed from the liquid air, is brittle and hard, but if it be exposed to heat it acquires great elasticity. A thread of 1 mm. diameter may be stretched to about six times its length and will then return to almost its original length. The sulphur, however, loses its elasticity about half an hour after it has been removed from the liquid air, and it becomes plastic although not permanently so. When elastic, the sulphur has a polished appearance and is quite transparent (P. P. Von Weimarn, J. Russ. Phys. Chem. Soc. 1910, 42, 474).

Molecular weight. This has been determined by measuring the molecular surface energy of sulphur dissolved, respectively, in carbon disulphide and in disulphur dichloride. In both solvents the molecular weight of sulphur corresponds with S_6 or S_8 molecules (Desiderius Pekar, Zeitsch. physikal. Chem. 1902, 39, 433). It has also been shown by Gerhard Preuner (*ibid*. 1903, 44, 733) that S_2 and S_4 molecules also exist. The curve representing the change of gas density at 448°, with change of pressure and also the calculation of the equilibrium constants of the experimental data, supply information as to the whole course of the dissociation which appears to justify this statement. The molecule, as determined by vapour density, is S_8 at low temperatures, but it commences to dissociate as the temperature is raised, and at 850° to 900° only S_2 molecules are left.

Specific gravity. Amorphous sulphur, 2·04; rhombic sulphur, 2·06; monoclinic sulphur, 1·96; molten sulphur, 1·801–1·815. At boiling-point (444·5°), 1·46–1·52.

Melting-point. Rhombic crystals, if pure and melted without being transformed, melt at 114·5°; prismatic crystals, if pure, melt at 120°. Plastic sulphur has no definite melting-point, increase of temperature merely diminishing viscosity and increasing the tendency for the sulphur to pass into the crystalline form (J. H. Kastle and W. P. Kelley, Amer. Chem. J. 1904, 32, 483).

Boiling-point. As determined on the constant air pressure thermometer, sulphur boils between 443·58° and 443·62° (N. Eumorfopoulos, Proc. Roy. Soc. 1908, A, 81, 339). According to Callendar and H. Moss (*ibid.* 1909, A. 83, 106) it boils at 444·5°.

Specific heat. Mean specific heat between 0° and 100° is 0·1712.

Ignition point. The ignition point, determined by means of a U tube through which air or oxygen is slowly drawn, is found to be 261° (255° uncorr.) in air at ordinary atmospheric pressure, and 257° to 264° (uncorr.) in oxygen (R. H. McCrae and A. Wilson, Chem. News, 1907, 96, 25).

The heat of combustion of sulphur burning to sulphur dioxide is 71,720 cal. for the monoclinic and 71,080 cal. for the rhombic variety (Thomsen, Thermochem. Unters. 2, 247).

Solubility. Sulphur is insoluble in water and only slightly soluble in alcohol, ether and ethereal oils. In carbon disulphide it is soluble to the extent of about 40 p.c. in the cold and about 182 parts are dissolved in 100 parts at 55°, which is the boiling-point of the saturated solution.

Sulphur dissolves freely in benzyl chloride. The solubility increases from 1 p.c. at 0° to 55·8 p.c. at 134°. It melts in benzyl chloride at 106·2° to 106·8°, and does not mix with the excess of solvent, but above 136° it mixes with benzyl chloride in all proportions (J. J. von Bojuski, J. Russ. Phys. Chem. Soc. 1905, 37, 92).

It is soluble in light petroleum; benzene and toluene dissolve about 26·4 parts at 100°. Tar oil dissolves about 50 p.c. at 100°. a-Sulphur is freely soluble in boiling acetic acid and also in boiling ethyl or methyl alcohol.

Combinations with oxygen, v. infra.

In addition to the references above quoted, the following may be cited: Amorphous Sulphur, by A. Smith and W. B. Holmes (Ber. 1902, 35, 2992); Amorphous Sulphur and its Relation to the Freezing Point of Sulphur, by A. Smith (Proc. Roy. Soc. 1902, 24, 299); Causes which Determine the Formation of Amorphous Sulphur, by A. Smith (*ibid.* 1902, 24, 342); Influence of Amorphous Sulphur on the Freezing Point of Liquid Sulphur, by A. Smith and W. B. Holmes (Zeitsch. physikal. Chem. 1903, 42, 469); Two Liquid States of Sulphur and their Transition Point, by A. Smith (Proc. Roy. Soc. 1905, 25, 588); Change of State of Liquid Sulphur, by F. Hoffmann and R. Rothe (Zeitsch. physikal. Chem. 1906, 55, 113); Vapour Pressure of Sulphur, by W. Matthies (Chem. Zentr. 1906, 2, 204); Surface Tension of Fused Sulphur, by H. Zickendraht (Ann. Chim. Phys. 1906 [iv.] 21, 141); Precipitated Sulphur, by R. H. Brownlee (J. Amer. Chem. Soc. 1907, 29, 1032); Changes in the Viscosity of Liquid Sulphur, by L. Rotinjanz (Zeitsch. physikal. Chem. 1908, 52, 609); Thiozonides, Sulphur and its Cyclic Compounds, by H. Erdmann (Annalen, 1908, 362, 133); Solubility of 'Insoluble' Sulphur, by A. Wigand (Zeitsch. physikal. Chem. 1910, 75, 235).

A. G. S.

HYDRIDES OF SULPHUR.

Sulphuretted hydrogen H_2S. This gas must have been known from very early times. It is described by the writers of the sixteenth and seventeenth centuries under the general name of 'sulphurous vapours.' Geber prepared milk of sulphur, but no mention is made of a fœtid-smelling gas being given off in the process. Scheele was the first, in 1777, to examine the gas minutely, and its chemical composition was definitely established by Berthollet.

Occurrence.—Sulphuretted hydrogen occurs in the gases issuing from volcanos, sometimes to the extent of 25 p.c. of their volume. It also occurs in the natural gas of Point Abino, Canada. Decaying vegetable substances, particularly the leguminous plants, peas, beans, and lentils, when heaped together in a moist condition evolve this gas, and it is also produced during the decomposition of animal substances such as blood, hair, flesh, &c. It is present in the hepatic waters of Harrogate, Aix-la-Chapelle, and other places. Decomposing organic matter in contact with sulphates frequently generates this gas, and from this cause sulphides are occasionally found at the mouths of large rivers which bring down much organic matter. The smell of sewer gas is in part due to sulphuretted hydrogen, and this latter also occurs in coal-gas, from which it has to be removed by a special arrangement in gas manufacture.

Preparation.—(1) It is usually prepared by the action of dilute sulphuric acid on ferrous sulphide $FeS+H_2SO_4=FeSO_4+H_2S$. It should be collected over hot water, in which it is less soluble than in cold. The gas obtained by this method is never pure, as the sulphide used contains small particles of metallic iron, which give rise to hydrogen. The gas should be washed in water to free it from acid or salt which may pass over. Excess of sulphuric acid causes the precipitation of white, anhydrous ferric sulphate which coats the sulphide and stops the evolution of gas.

(2) A purer gas is obtained by heating antimony sulphide with hydrochloric acid of sp.gr. 1·1; $Sb_2S_3+6HCl=2SbCl_3+3H_2S$. If native antimony sulphide be used, it should be first treated with dilute hydrochloric acid to decompose any carbonates which may be present.

(3) The gas may be prepared on a large scale by heating a mixture of equal parts of sulphur and paraffin, vaseline, or many other organic bodies.

(4) By heating a damp mixture of sulphur and charcoal.

(5) Sulphuretted hydrogen is formed together with sulphur dioxide when steam is passed over boiling sulphur, or even when sulphur is boiled with water; $3S+2H_2O=2H_2S+SO_2$. The two gases thus obtained mutually decompose one another, so that only a portion of the sulphuretted hydrogen remains, and sulphur is deposited.

(6) By the decomposition of aluminium sulphide by water

$$Al_2S_3+6H_2O=Al(OH)_3+3H_2S.$$

(7) By passing dry hydrogen over certain heated sulphides, such as powdered antimony sulphide; $Sb_2S_3+3H_2=Sb_2+3H_2S$. The gas is also formed by passing a current of hydrogen through boiling sulphur; by burning a jet of hydrogen in sulphur vapour, and by burning sulphur in an atmosphere of hydrogen.

(8) Pure H_2S may be prepared by passing

the impure gas first through a drying apparatus and then through a series of vessels cooled by liquid air, in which it is solidified. When a sufficient amount has been collected, all residual gas is drawn out of the apparatus by means of a pump, and the condensed H_2S is then allowed to boil, the first 500 c.c. being rejected. The gas so obtained is completely absorbed by alkalis (Moissan, Compt. rend. 1903, 137, 363).

Properties.—Sulphuretted hydrogen is a colourless, inflammable gas, possessing a most disagreeable smell, resembling that of rotten eggs, which is due in part, when the gas has been prepared from ferrous sulphide, to volatile sulpho-carbon compounds derived from the iron. It has a sp.gr. of 1·1895 (Leduc), and 1 litre at 0° and 760 mm., weighs 1·5392 grms. It burns with a pale-blue flame, forming water and sulphur dioxide, and usually depositing more or less sulphur—

$$H_2S+3O=SO_2+H_2O$$
$$SO_2+2H_2S=2H_2O+3S.$$

A mixture of two volumes of sulphuretted hydrogen and three volumes of oxygen explodes violently when an electric spark is passed through it, complete combustion taking place.

The gas when inhaled acts as a powerful poison, producing asphyxia; even in small quantities it causes sickness and headache. According to Thénard, an atmosphere containing $\frac{1}{800}$ of its volume of this gas will kill a dog, and smaller animals die with even less than that amount. An atmosphere with $\frac{1}{250}$ part of H_2S is sufficient to kill a horse, while cold-blooded animals are not affected by this proportion of gas. The best antidote is the inhalation of very dilute chlorine obtained by moistening a towel with dilute acetic acid, and sprinkling bleaching powder upon it.

Sulphuretted hydrogen is soluble in water, one volume of this liquid dissolving about 4·4 volumes of the gas at 0°, and 3·2 volumes at 15°. The solubility at other temperatures is given by the expression

$$c=4{\cdot}4015-0{\cdot}089117t+0{\cdot}00061954t^2$$

(Henrich, Zeitsch. physikal. Chem. 9, 435).

Alcohol dissolves 17·89 times its volume of the gas at 0°. The aqueous solution of the gas reddens blue litmus, and possesses the peculiar smell and taste of the gas. The solution decomposes on standing, the hydrogen combining with the oxygen of the air to form water, while sulphur deposits, imparting a milky appearance to the liquid. A solution of the gas in glycerol keeps better, and is occasionally used as a reagent.

A hydrate of sulphuretted hydrogen, of the formula $H_2S,7H_2O$, has been described by Forcrand (Compt. rend. 1902, 134, 281), and a series of mixed hydrates of the type

$$M,2H_2S,23H_2O,$$

where M is a volatile organic halogen compound, have also been prepared.

Sulphuretted hydrogen is decomposed by almost all oxidising agents. The halogens unite with its hydrogen, liberating sulphur

$$H_2S+Cl_2=2HCl+S.$$

(The reaction with iodine only takes place in the presence of water.) Fuming nitric acid, dropped into a jar of the gas, decomposes it with explosive violence. Sulphuric acid is decomposed by H_2S forming S, SO_2, and polythionic acids, hence it cannot be used for drying the gas. On account of its ready oxidisability, sulphuretted hydrogen is occasionally employed in organic chemistry as a mild reducing agent. Sulphuretted hydrogen is easily decomposed by heat; according to Myers (Annalen, 159, 124) decomposition commences at a temperature of 400°. When a spiral of platinum is heated in the gas, sulphur is deposited and hydrogen liberated, which occupies the same volume as the original gas. The dissociation at various temperatures has been studied by Preuner (Zeitsch. anorg. Chem. 1907, 55, 279).

Sulphuretted hydrogen acts on most metals and many metallic oxides, forming sulphides; thus silver and mercury are immediately tarnished in contact with the gas. The sulphides are also formed when the gas is passed through solutions of many metallic salts as insoluble precipitates, several of which possess characteristic colours. Thus cadmium sulphide is yellow, antimony sulphide orange, and stannous sulphide chocolate-brown. Hence sulphuretted hydrogen is largely used in analytical operations, a current of the gas being passed through the solution under examination. Paper impregnated with a solution of a lead salt, *e.g.* the acetate, is used as a test for H_2S, such paper being blackened in contact with sulphuretted hydrogen. For the same reason, paintings containing white lead are darkened by exposure to the air of towns, while cards glazed with white lead, and engravings on paper whitened with that substance suffer similarly.

The sulphuretted hydrogen occurring in coal gas may be removed by passing the gas over hydrated ferric oxide

$$2Fe(OH)_3+3H_2S=2FeS+S+6H_2O.$$

Sulphuretted hydrogen may be liquefied by pressure; its critical temperature and pressure are 100° and 90 atmospheres respectively. At the ordinary temperature a pressure of 17 atmospheres condenses it to a colourless, mobile liquid, of sp.gr. 0·9. The liquid boils at −61°, and freezes to an ice-like solid at −82·9°. The density of the liquid at its b.p. is 0·964. Liquid H_2S can also be obtained by cooling the gas to about −70° with a mixture of solid carbon dioxide and ether, or by sealing up a quantity of hydrogen persulphide in one limb of a V-shaped glass tube. The persulphide slowly decomposes, and the pressure eventually becomes sufficient to liquefy the sulphuretted hydrogen produced. The chemical activity vanishes almost entirely when the gas is liquefied; metallic potassium and sodium are unchanged in contact with the liquid, and it is also without action on chromates and permanganates.

Small amounts of H_2S in mineral waters may be detected by adding to the water a few c.c. of hydrochloric acid, stirring in a little solid *p*-aminodimethylaniline, and then adding a drop of ferric chloride. If H_2S be present a blue colour (methylene blue) will develop. This reaction will detect 0·018 mgm. of H_2S in a litre of water.

Salts. A solution of sulphuretted hydrogen in water acts as a weak acid, whence the name sometimes given to it of 'hydrosulphuric acid.' It forms two series of salts, the sulphides R_2S and the hydrosulphides RHS. Of this latter class only the salts of the alkalis and alkaline earths are known; they are produced by the action of an excess of sulphuretted hydrogen on the oxides or hydroxides of these metals.

The normal sulphides can be obtained by the following methods—

(1) By the direct union of a metal, *e.g.* Fe with sulphur at a high temperature.

(2) By the action of sulphur on certain metallic oxides, SO_2 being evolved.

(3) By the reduction of sulphates with carbon.

(4) By the action of CS_2 on some metallic oxides, *e.g.* Cr_2O_3 at about 250°.

(5) By the action of sulphuretted hydrogen on a metallic oxide or salt.

Besides the normal sulphides, many polysulphides of the type R_2S_2, R_2S_3, R_2S_4, &c., exist. Those of the alkalis and alkaline earths can be prepared by boiling a solution of the normal sulphide with an excess of sulphur. All the sulphides except those of the alkalis and alkaline earths are insoluble in water; many are decomposed by dilute acids with evolution of sulphuretted hydrogen. Many sulphides, *e.g.* those of lead, copper, and zinc, occur native as minerals and constitute important ores.

Uses. Sulphuretted hydrogen is employed on the large scale to remove arsenic from sulphuric acid, for precipitating copper from solutions of the salts of that metal, and for precipitating gold and silver from waste material containing them. It is also largely employed in the laboratory in analytical operations.

HYDROGEN PERSULPHIDES.

Hydrogen persulphide was discovered by Scheele in 1777, and more completely investigated by Berthollet. It was first obtained by pouring a concentrated solution of potassium pentasulphide into dilute, ice-cold hydrochloric acid, when, on standing for some time, yellow drops of a transparent, oily liquid separated out. Berthollet believed it to be analogous in composition to the potassium sulphide used in its preparation, and assigned to it the formula H_2S_5. Thénard, however, who found it possessed many properties in common with hydrogen peroxide, gave it the formula H_2S_2, though his analyses always showed a larger proportion of sulphur than is demanded by this formula. Hofmann, who obtained it by decomposing with hydrochloric acid a crystalline compound formed by the action of ammonium persulphide on strychnine, believed it to possess the formula H_2S_3. It has been shown that the so-called 'hydrogen persulphide,' hitherto obtained is really a mixture of a di- and tri-sulphide (Schenck and Falcke, Ber. 1908, 41, 2600).

Preparation. A solution of sodium or calcium polysulphide is carefully poured into an equal volume of concentrated hydrochloric acid, kept well cooled by ice. A heavy, yellowish oil separates out, which is then submitted to distillation under reduced pressure. The di- and tri-sulphides are separated by fractional distillation. Care must be taken to remove all traces of alkali from the distillation apparatus by previously treating it with sulphuric acid, as the hydrogen persulphides are very readily decomposed by even traces of alkali.

Hydrogen disulphide H_2S_2. The disulphide thus obtained is an oil, boiling at 74°–75° (2 mm.) of sp.gr. 1·376. It is more volatile than the trisulphide, and not so readily attacked by alkalis.

Hydrogen trisulphide H_2S_3. Hydrogen trisulphide forms a colourless, strongly refracting liquid of sp.gr. 1·496 at 15°. It boils at 43°–50° (4½ mm.), and solidifies at about −53°. It has an odour resembling that of camphor, and decomposes slowly in the dark, more rapidly on exposure to light, evolving H_2S and depositing sulphur. It dissolves in many organic solvents without decomposition, and its solutions in ether, benzene, and carbon disulphide are relatively stable (Schenck and Falcke, *l.c.*). It forms a well-crystallised compound with benzaldehyde of the composition

$$(C_6H_5{\cdot}CHO)_2,H_2S_3$$

(Brunner and Vuilleumier, Chem. Zentr. 1908, ii. 588).

HALOGEN COMPOUNDS OF SULPHUR.

The affinity of sulphur for the halogens decreases rapidly from fluorine to iodine. The hexafluoride is a very stable compound, while the only well-defined chloride is S_2Cl_2, the tetrachloride being easily decomposed. The only known compound of sulphur and bromine has the formula S_2Br_2, whilst no iodide is known, all the compounds previously classed as such (with the possible exception of S_3I_2) being merely mixtures of sulphur and iodine.

Sulphur hexafluoride SF_6. This body was discovered in 1900 by Moissan and Lebeau, who obtained it by the direct union of sulphur and fluorine (Compt. rend. 1900, 130, 865). It possesses a theoretical interest as being the first hexahalogen derivative of sulphur to be prepared. It is a colourless, inodorous, incombustible gas, condensible to a liquid at a low temperature (b.p. about −57°). It is slightly soluble in water, rather more so in alcohol. Chemically, it is a very inert body, but it is slowly decomposed when mixed with hydrogen and submitted to a powerful spark discharge, producing HF, H_2S and S, and it is also attacked by sodium or calcium vapour at a red heat.

Sulphur chlorides. Only two chlorides of sulphur are definitely known, *i.e.* S_2Cl_2 and SCl_4. An intermediate chloride SCl_2 was formerly thought to exist, but later work points to its being merely a solution of chlorine in S_2Cl_2 (Ruff and Fischer, Ber. 1903, 36, 418; *see*, however, Beckmann, Zeitsch. physikal. Chem. 1909, 65, 289).

Sulphur monochloride S_2Cl_2. This chloride was first obtained by Hagemann in 1781, but its composition was not fully established until the year 1810, when it was studied by Davy and Bucholz.

Preparation. Sulphur monochloride may be obtained by passing dry chlorine gas over melted sulphur, and distilling the chloride from the excess of sulphur. The chlorine is generated in the ordinary way, and passed through a wash bottle containing water, then through calcium chloride, and thence over melted sulphur contained in a retort. The chloride of sulphur is condensed in a receiver cooled by a stream of cold water. On the large scale, sulphur monochloride is obtained as a by-product in the preparation of carbon tetrachloride from carbon disulphide and chlorine: $CS_2+3Cl_2=CCl_4+S_2Cl_2$.

Properties. Sulphur monochloride is an amber-coloured liquid which fumes strongly in moist air, and possesses a peculiarly penetrating smell, its vapours attacking the mucous membrane. Its sp.gr. is 1·70941 at 0°/4° (Thorpe), m.p. −75° to −76° (Beckmann), and b.p. 138·1°. Water slowly decomposes it, forming at first sulphur, hydrochloric acid, and thiosulphuric acid, this latter then further splitting up into sulphur and sulphurous acid

$$2S_2Cl_2+3H_2O=4HCl+S_2+H_2S_2O_3, \text{ and}$$
$$H_2S_2O_3=S+H_2SO_3.$$

Sulphur monochloride is easily soluble in benzene and carbon disulphide. It readily dissolves sulphur, and the saturated solution contains at ordinary temperatures 66·7 p.c. of sulphur. It acts on many metals, *e.g.* iron, tin, aluminium, and mercury, producing chlorides (Nicolardot, Compt. rend. 1908, 147, 1304), and most metallic oxides yield chlorides when heated in its vapour. This latter reaction affords a means of preparing certain chlorides free from oxychlorides (Bourion, *ibid.* 1909, 148, 170). Sulphur monochloride acts on many organic compounds to form sulpho derivatives; for example, with benzene it yields (in the presence of aluminium chloride) phenyl sulphide $(C_6H_5)_2S$. This reaction affords support to the formula $S{=}SCl_2$ for the chloride (Böeseken, Chem. Soc. Abstr. 1905, i. 583). Hicks (J. Amer. Chem. Soc. 1911, 38, 1492) has utilised sulphur monochloride for the decomposition of minerals containing rare earths, by heating them in a current of the vapour.

Uses. Sulphur monochloride is used in defecating cane-juice and refining sugar, in the so-called Eastes' process. Its principal application is, however, for vulcanising india-rubber.

The articles to be vulcanised are first coated with india-rubber in the usual way, and are then placed in a closed chamber in which sulphur chloride is vapourised, by which means the vulcanisation of the india-rubber is effected (Abbot, Eng. Pat. 1878, 166).

Parkes' process, which has been in use since 1846, consists in immersing the india-rubber goods in a solution of sulphur chloride (saturated with sulphur) in carbon disulphide or benzene for a short time. It is used extensively in preparing the surface of tobacco pouches, tubing, rings, &c.

Sulphur tetrachloride SCl_4. Sulphur tetrachloride is formed by saturating the monochloride with chlorine at a temperature of −20°. It forms a brown-red liquid, which on being strongly cooled freezes to a yellowish-white solid, of m.p. −31°. On removal from the freezing mixture the tetrachloride at once commences to decompose, evolving chlorine. Water decomposes it violently, forming sulphurous and hydrochloric acids $SCl_4+2H_2O=SO_2+4HCl$.

Sulphur tetrachloride forms well-defined crystalline double chlorides with many metallic chlorides, such as $SbCl_5,SCl_4$, $FeCl_3,SCl_4$, &c. (Ruff, Ber. 1904, 37, 4513).

Sulphur bromide. Sulphur monobromide S_2Br_2 is formed by direct union of its elements when sulphur is dissolved in a slight excess of bromine, and the excess of the latter then removed by a current of dry CO_2. It is a ruby-red liquid, which boils at about 210°, and can be completely separated into its constituents by repeated distillation. Water decomposes it in a similar manner to S_2Cl_2. Caustic potash acts on it, giving a mixture of potassium bromide and sulphite with liberation of sulphur.

Determinations of the melting-points and vapour densities of mixtures of S_2Br_2 and bromine have failed to show the formation of any other compounds of bromine and sulphur (Ruff and Winterfeld, Ber. 1903, 36, 2437).

Sulphur iodide. A compound of the composition S_2I_2 has been described as obtained by the action of sulphuretted hydrogen on a solution of iodine chloride, the current of gas being stopped before the whole of the chloride was decomposed (MacIvor, Chem. News, 1902, 86, 5).

Other observers have, however, made detailed studies of the system sulphur-iodine, and rendered it probable that the above body is really only a mixture of sulphur and iodine, as no evidence of the formation of any compounds of the two elements could be obtained; *see* Boulouch, Compt. rend. 1903, 136, 1577; Smith and Carson, Zeitsch. physikal. Chem. 1907, 61, 200; Ephraim, Zeitsch. anorg. Chem. 1908, 58, 338; Olivari, Chem. Soc. Abstr. 1909, ii. 37.

OXYHALOGEN COMPOUNDS OF SULPHUR.

Two series of compounds of this class are known, corresponding to the two oxides of sulphur SO_2 and SO_3. The former class are termed thionyl, and the latter sulphuryl compounds.

Thionyl fluoride SOF_2, prepared by heating arsenic fluoride with thionyl chloride in a sealed tube at 100°, is a colourless gas with an odour like carbonyl chloride, liquefying at −32°. Water decomposes it into hydrofluoric and sulphurous acids.

Thionyl chloride $SOCl_2$ was first obtained in an impure state by Persoz and Block, and more fully investigated by Carius. It may be prepared by the action of dry sulphur dioxide on phosphorus pentachloride

$$SO_2+PCl_5=SOCl_2+POCl_3.$$

Other methods of preparation consist in the action of PCl_5 on thiosulphates, sulphites, and dithionates, and the direct union of chlorine monoxide with sulphur dissolved in carbon disulphide.

Thionyl chloride is a colourless, strongly-fuming, pungent-smelling liquid, of sp.gr. 1·675 at 0°. It boils at 78°, and on heating to 440°, splits up into sulphur monochloride, sulphur dioxide, and chlorine. Water decomposes it, giving sulphurous and hydrochloric acids. It acts on oxygen acids as a chlorinating agent; thus with sulphuric acid it yields chlorsulphonic acid. On account of the ease with which it parts with its chlorine it is employed in organic chemistry in preparing chloro-derivatives from certain hydroxy acids. It also acts on many organic aldehydes, *e.g.* piperonal, forming dichlorides, but the method is not of general application (Hoering and Baum, Ber. 1908, 41, 1914). Thionyl chloride may be made technically by adding SO_3 to S_2Cl_2 at a temperature of 75°–80°

$$SO_3+S_2Cl_2=SOCl_2+SO_2+S.$$

Chlorine is passed continuously into the product to reconvert the sulphur into chloride, and a nearly theoretical yield of thionyl chloride can thus be obtained (Chem. Fab. Griesheim Elektron Chem. Soc. Abstr. 1903, ii. 420).

Thionyl bromide $SOBr_2$ has been prepared from thionyl chloride and sodium bromide by Hartog and Sims (Chem. News, 1893, 67, 82). It is an orange-yellow liquid, boiling at 68°, and of sp.gr. 2·61 at 0°.

Thionyl chlorobromide $SOBrCl$, prepared from thionyl chloride and hydrobromic acid, is a clear yellow liquid of sp.gr. 2·31 at 0°, boiling at 115° with slight decomposition (Besson, Compt. rend. 1896, 122. 320).

Sulphuryl fluoride SO_2F_2 is obtained by the direct union of sulphur dioxide and fluorine. It is a gas, colourless and odourless, which liquefies at −52°, and solidifies at −120°. It dissolves in water without undergoing decomposition, and attacks glass. Alkalis decompose it, forming sulphurous and hydrofluoric acids (Moissan and Lebeau, Compt. rend. 1901, 132, 374).

Sulphuryl chloride SO_2Cl_2. This body was discovered by Regnault in 1838, who obtained it by acting with chlorine on a mixture of ethylene and sulphur dioxide. It is best prepared by passing well-dried chlorine and sulphur dioxide simultaneously into a large glass flask containing some camphor which has previously been saturated with sulphur dioxide. Care must be taken that the chlorine is never in excess. The two gases combine to form sulphuryl chloride, the camphor remaining unaltered. The product is rectified, and the portion boiling at 70°–72° collected separately. Formic acid can be used in place of the camphor. Sulphuryl chloride is a colourless liquid, b.p. 69·2°, sp.gr. 1·7045 at 0°. A small quantity of water converts it into chlorsulphonic acid, but a larger quantity decomposes it entirely, into sulphuric and hydrochloric acids

$$SO_2Cl_2+2H_2O=H_2SO_4+2HCl.$$

Added in small portions to ice-cold water, sulphuryl chloride forms a crystalline hydrate, stable at 0° (Baeyer and Villiger, Ber. 1901, 736).

On heating it splits up into SO_2 and Cl_2, the dissociation being complete at about 450°. On account of the ease with which it dissociates it acts as a powerful chlorinating agent, and has been patented for this purpose (for preparing the chlorides and anhydrides of organic acids)

$$2RCOONa+SO_2Cl_2=Na_2SO_4+2ROCl, \text{ and}$$

$$4RCOONa+SO_2Cl_2 =Na_2SO_4+2NaCl+2\genfrac{}{}{0pt}{}{R{\cdot}CO}{R{\cdot}CO}{>}O.$$

Pyrosulphuryl chloride $S_2O_5Cl_2$ is produced by the action of sulphur trioxide on sulphur monochloride, phosphorus pentachloride, and other chlorine compounds. It is best prepared by acting on fuming sulphuric acid with carbon tetrachloride, a method first introduced by Schützenberger; $2SO_3+CCl_4=COCl_2+S_2O_5Cl_2$. The carbon tetrachloride is placed in a flask fitted with a reflux condenser, and the oleum slowly added through a tap funnel. The flask is heated for some time after the evolution of phosgene has ceased, and the contents are then fractionated. The crude pyrosulphuryl chloride, thus obtained, is purified by the addition of fused sodium chloride and redistillation under reduced pressure, the sodium chloride combining with the chlorsulphonic acid present to form a salt, which remains behind in the distilling flask.

Pyrosulphuryl chloride is a colourless, fuming liquid, of sp.gr. 1·872 at 0°. It boils at about 153° at the ordinary pressure with slight decomposition, but may be distilled unchanged under 19 mm. pressure. It is slowly decomposed by water with formation of chlorosulphonic acid, which in turn yields hydrogen chloride and sulphuric acid as final products.

Fluorsulphonic acid $SO_2{<}\genfrac{}{}{0pt}{}{F}{OH}$ is formed by the direct union of sulphur trioxide with hydrogen fluoride at a low temperature. It is a colourless, mobile liquid, boiling at 162·6°, with slight decomposition (Thorpe and Kirman, Chem. Soc. Trans. 1892, 61, 921).

Chlorsulphonic acid $SO_2{<}\genfrac{}{}{0pt}{}{Cl}{OH}$. This compound was first obtained by Williamson by the direct union of sulphur trioxide and hydrogen chloride, and by distilling a mixture of sulphuric acid and phosphorus oxychloride

$$2SO_2{<}\genfrac{}{}{0pt}{}{OH}{OH}+POCl_3=2SO_2{<}\genfrac{}{}{0pt}{}{Cl}{OH}+HPO_3+HCl$$

It is best prepared by the first-named reaction, by passing well-dried hydrogen chloride into fuming sulphuric acid until no further absorption takes place. The contents of the flask are then distilled in a current of dry hydrogen chloride, and the portion boiling at 145°–160° collected separately. The product thus obtained may be further purified by redistillation, but if required perfectly pure must be crystallised several times at a low temperature. The melting-point of the pure acid is −80°.

It had a special importance at the time of its discovery, as it was the first example of a substance to be referred to mixed types.

$$\begin{matrix}\text{Mixed water}\\ \text{type}\end{matrix}\quad \begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}O\\ HCl\end{matrix}\qquad\qquad \begin{matrix}\text{Chlorsulphonic}\\ \text{acid}\end{matrix}\quad \begin{matrix}H\\ SO_2{<}\end{matrix}\!\!\begin{matrix}\}O.\\ Cl\end{matrix}$$

It is a colourless, fuming liquid of sp.gr. 1·784 at 0°, and boils with slight decomposition at 151°–152°. Its vapour dissociates on heating, the decomposition being complete at 200°. $2SO_2{<}\genfrac{}{}{0pt}{}{Cl}{OH}=SO_2+Cl_2+H_2O+SO_3$. At a red heat the products are sulphur dioxide, steam, and chlorine (Ruff, Ber. 1901, 34, 3509).

Chlorsulphonic acid is decomposed by water with explosive violence, forming hydrochloric and sulphuric acids, and when added to strong sulphuric acid, disulphuric acid and hydrochloric acids are formed

$$SO_2{<}\genfrac{}{}{0pt}{}{OH}{Cl}+SO_2{<}\genfrac{}{}{0pt}{}{OH}{OH}=\begin{matrix}SO_2{<}OH\\ \quad{>}O\\ SO_2{<}OH\end{matrix}+HCl$$

With finely divided tellurium and selenium chlorsulphonic acid gives a cherry-red and a moss-green colour respectively. On standing for a considerable time the liquid becomes colourless.

Chlorsulphonic acid acts on many organic bodies with formation of sulpho derivatives, and hence is often employed in the preparation of these compounds.

For an account of the literature on chlorsulphonic acid and pyrosulphuryl chloride, *v.* Sanger and Riegel, Proc. Amer. Acad. of Arts and Sciences, 1912, 47, 18.

Oxides and Oxyacids of Sulphur.

Sulphur dioxide SO_2. The ancients knew that when sulphur was burnt it evolved pungent fumes, and these fumes have long been used for fumigating purposes and for purifying cloth. It was formerly supposed that sulphuric acid was produced by burning sulphur in the air, but Stahl proved the fallacy of this idea; the gas was then known as phlogisticated vitriolic acid, in accordance with the views of that time. Priestley in 1775 first prepared the pure gas.

Occurrence. Sulphur dioxide occurs among the gases issuing from volcanos, and in a state of solution in the waters of certain volcanic springs. It also occurs to a small extent in the air of towns, being mainly derived from the pyrites contained in coal.

Preparation. (1) By burning sulphur in air or oxygen. The sulphur ignites at a temperature of about 250°–260°, and sulphur dioxide is obtained equal in volume to that of the oxygen consumed: $S+O_2=SO_2$.

(2) By roasting pyrites. This method is mainly employed in the manufacture of sulphuric acid on the large scale.

(3) By heating a mixture of manganese dioxide and sulphur: $MnO_2+S_2=MnS+SO_2$.

(4) By the action of warm, dilute sulphuric acid on sulphites, as sodium sulphite

$$Na_2SO_3+H_2SO_4=Na_2SO_4+H_2O+SO_2.$$

(5) By heating sulphuric acid with certain deoxidising substances, such as sulphur and charcoal

$$S+2H_2SO_4=2H_2O+3SO_2$$
$$C+2H_2SO_4=2H_2O+CO_2+2SO_2.$$

This latter reaction has been employed on the large scale in the manufacture of alkaline sulphites; the carbon dioxide simultaneously evolved is not detrimental, as it is almost insoluble in water containing sulphurous acid.

Properties. Sulphur dioxide at ordinary temperatures is a colourless, irrespirable, incombustible gas, of sp.gr. 2·2639 (air 1). 1 litre of the gas at 0° and 760 mm. weighs 2·9266 grms. It may be collected by downward displacement like carbon dioxide, but if required quite free from air should be collected over mercury. It possesses the well-known smell of burning sulphur. Sulphur dioxide is very soluble in water, the solution being accompanied by a slight rise in temperature. At 0° water dissolves 79·79 times its volume of the gas, at 20° 39·37 volumes, and at 40° 18·77 volumes, prolonged ebullition being required to expel the last traces of the gas from the solution (Bunsen and Schoenfeld, Annalen, 95, 2). The solution of the gas has a strongly acid reaction, reddens blue litmus, and afterwards bleaches it, but the perfectly dry gas has not these properties. The gas is also soluble in alcohol, and in strong sulphuric acid, this last liquid taking up at ordinary temperatures 58 times its own volume of SO_2. By cooling a saturated solution of the gas in water, a number of hydrates containing 5, 8, 10, and 14 molecules of water have been obtained. They are colourless, crystalline bodies which melt at about 4°, and evolve SO_2 slowly on exposure to air. Sulphur dioxide is poisonous; $\frac{1}{2500}$ part in air causes dyspnœa, and affects the eyes. It is absorbed by the blood, and transformed in the system into sulphuric acid. Sulphur dioxide, both as a gas and in solution, is a powerful bleaching agent, and is used in bleaching those materials which would be injured by chlorine; this property was known to Paracelsus. The bleaching action of sulphur dioxide is a reducing one, whilst that of chlorine is an oxidising one; thus sulphur dioxide in the presence of moisture is oxidised to sulphuric acid, the liberated hydrogen reducing the colouring matter to a colourless compound. The colouring matters are probably in many cases not destroyed by the acid, but reduced to colourless leuco compounds, for in time the original colour often reappears, as in the case of bleached straw and flannel, which become yellow with age. Sulphur dioxide and sulphuretted hydrogen mutually decompose one another in the presence of moisture, with decomposition of sulphur and formation of water and polythionic acids (Wackenroder's solution). When sulphur dioxide and oxygen or air are passed over heated spongy platinum, the two gases combine to form sulphur trioxide. The platinum can be replaced by other substances, and the sulphur trioxide so produced is now used commercially in the manufacture of sulphuric acid (*see* under Sulphuric acid). With ammonia gas sulphur dioxide forms various compounds, according as the one or other gas is in excess. With an excess of SO_2, aminosulphinic acid $NH_2{\cdot}SO_2H$ is always formed, but with excess of ammonia either white $NH_2{\cdot}SO_2NH_4$ or red $NH_4N(SO_2NH_4)_2$ are obtained (*see* Divers and Ogawa, Chem. Soc. Trans. 1901, 79, 1102; Ephraim and Pistrowski, Ber. 1911, 44, 379). Many metals are attacked when heated in the gas; potassium burns with formation of potassium thiosulphate and sulphite, and tin and finely divided iron are changed partly into sulphides and partly into oxides. When the gas is passed over metallic peroxides, *e.g.* lead peroxide, sulphates are formed, often with considerable evolution of heat. Sulphur dioxide is a strong reducing agent, being readily converted into sulphuric acid by addition of oxygen; the halogens are converted by it into the halogen acids, and solutions of the noble metals are reduced with precipitation of the metal. At a temperature of about 1200° sulphur dioxide is decomposed into sulphur and oxygen, part of the latter combining with a portion of the undecomposed sulphur dioxide to form the trioxide. The same decomposition takes place when electric sparks are passed through the gas, but the decomposition is only complete when the sulphur trioxide is removed as soon as formed by absorption with sulphuric acid. Tyndall has shown that the gas is also decomposed by passing a beam of sunlight through a long tube filled with the gas, when a white cloud is formed, consisting of sulphur trioxide.

The composition of sulphur dioxide is ascertained by burning sulphur in a flask of oxygen inverted over mercury. The sulphur is placed in a cup inside the flask, and is so arranged that the sparks from an induction coil, on passing between wire terminals come in contact with, and ignite the sulphur. The volumes of oxygen before the combustion and of sulphur dioxide after combustion, are found to be the same.

Liquid sulphur dioxide. Sulphur dioxide is condensible to a liquid at the temperature obtainable by a mixture of ice and salt, or by a pressure of about 2½ atmospheres at ordinary temperatures. Its critical temperature is 156°, and critical pressure 78·9 atmospheres. The liquid acid is a colourless, mobile fluid, of sp.gr. 1·4338. It boils at −10°, and on being cooled solidifies to a white mass melting at −72·7°. The liquid oxide dissolves many salts and organic bodies and acts as a dissociating medium when used as a solvent in cryoscopic molecular weight determinations. It is miscible with many organic liquids, such as carbon disulphide and chloroform. With potassium iodide at temperatures below 0°, it forms a compound $KI(SO_2)_4$, and the formation of similar compounds has also been observed in the case of other salts. If free from water it has no action on iron, hence the liquid oxide can be transported in wrought iron cylinders. Owing to the rapid increase in the pressure of the SO_2 with rise of temperature, these must only be seven-eighths filled. The pressure in atmospheres of SO_2 at various temperatures is given below—

Pressure	Temperature	Pressure	Temperature
0	−10°	3·51	30°
0·53	0°	5·15	40°
1·26	+10°	7·18	50°
2·24	20°		

The liquid oxide is now sold in glass syphons, fitted with a screw valve, so arranged that either the liquid oxide or the gas may be obtained as desired, the current of gas being capable of adjustment to any desired speed by regulating the screw. A single syphon will evolve 500 litres of gas. Sulphur dioxide can be employed in the artificial production of low temperatures; a mixture of 3 p.c. CO_2 and 97 p.c. SO_2 was employed by Pictet for this purpose. This mixture boils at −19°. The low temperature of −140° is obtained by the evaporation of a solution of solid carbon dioxide in liquid sulphur dioxide, and has been utilised in the liquefaction of oxygen and nitrogen.

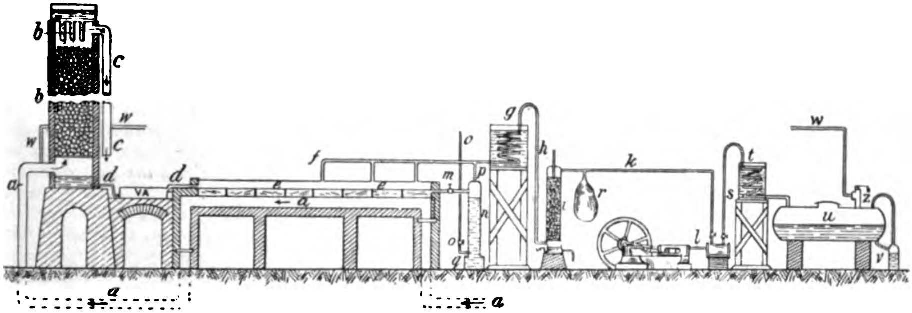


FIG. 1.

Detection of sulphur dioxide. For this purpose paper steeped in a solution of potassium iodate and starch is brought into the gas under examination, when a blue colour is at once produced if only traces of sulphur dioxide are present, iodide of starch being formed

$$2KIO_3+5SO_2+4H_2O=2I+2KHSO_4+3H_2SO_4$$

When the sulphur dioxide is in excess the blue paper is again bleached, hydriodic acid being formed

$$2I+SO_2+2H_2O=2HI+H_2SO_4.$$

This latter reaction is utilised in determining the amount of sulphur dioxide present in a solution. The solution under examination is placed in a burette and run into standard iodine solution containing a little starch paste, until the blue colour of the liquid disappears. The reverse process—running the iodine into the SO_2 solution—is not applicable, as in this case the action proceeds partly according to the following equation

$$SO_2+4HI=4I+2H_2O+S$$

the hydriodic acid formed reducing a part of the sulphurous acid to free sulphur.

Commercial manufacture of sulphur dioxide. The action of sulphuric acid on sulphur and charcoal is used only in the production of an aqueous solution of the gas. Liquid sulphur dioxide was first produced on a large scale by Pictet, who prepared the gas from sulphur and sulphuric acid in an iron retort lined with firebricks, cooled it to −10°, when all the moisture separated out in the form of hydrates, and compressed the residual dry gas with a pump. This process, however, is now superseded by that of Hanisch and Schröder. By means of this process, liquid SO_2 can be manufactured in a pure condition directly from the gases obtained by roasting zinc blende; these gases contain about 6–7 p.c. of SO_2. The method adopted is as follows, Fig. 1 being a sketch of the apparatus employed.

The gases from the roasting furnaces pass through the channel *a* under the leaden pans *e, e*, and in so doing part with their heat to these. They then enter the tower *b*, packed with coke or firebrick, down which a stream of cold water trickles. Practically complete absorption of the sulphur dioxide takes place, the residual air escaping through the pipe *c*. The aqueous solution of sulphur dioxide which collects at the bottom of the tower runs through the preliminary heater VA, composed of thin plates of lead around which hot waste liquors from a subsequent stage of the process circulate. The temperature of the issuing liquid is thus raised to about 85°. The liquid next runs over the lead pans *e, e*, and its temperature is raised to boiling by the heat of the flue gases passing underneath. The expelled sulphur dioxide passes through the pipe *f* to the worm *g*, where it is cooled and most of the accompanying moisture deposited. The last traces of moisture are removed by passage through the tower *i*, packed with coke, down which concentrated sulphuric acid trickles. The perfectly dry gas passes on through *k* (*r* is a taffeta bag to regulate the pressure), into the pump *l*, which is made of bronze. The gas is forced through *s* into *t*, where it is liquefied (for which a pressure of 2–3½ atmospheres is necessary, according to the season of the year). The liquefied gas then passes into the wrought-iron vessel *u*, whence it is drawn off as required, into small iron cylinders *v*. In order to recover the sulphur dioxide which remains in the liquid running away from the pans *e*, *e*, it is run into the small tower *n*, packed with lead wire. Steam is blown in through the pipe *o*, the remaining sulphur dioxide is completely expelled, and passes along with some steam into *g*, and the boiling water which collects at the bottom of *n* is used to circulate round the plates of the heating apparatus VA.

The pans *e*, *e*, are frequently omitted in practice, and the preliminary heater VA connected direct with the tower *n*. Instead of a simple worm, a tower (*see* Fig. 2) may be used for depriving the sulphur dioxide of the greater part of its moisture. The upper part of this tower is packed with coke, the lower half filled with perforated stoneware plates; the moist gas enters at the bottom, whilst a stream of water is run in at the top. By carefully adjusting the proportions of water and gas, boiling water collects at the bottom of the tower, whilst a steady stream of practically dry sulphur dioxide escapes through the tube *d*.

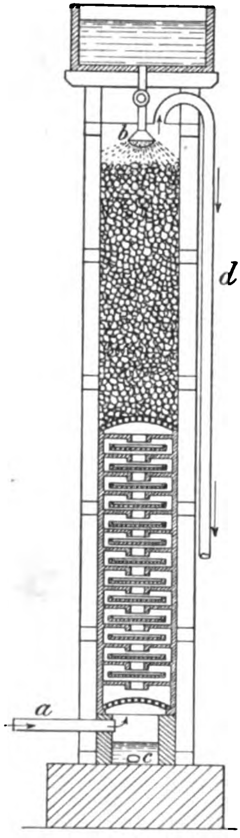


Fig. 2.

For this process to be successfully worked a minimum percentage of 4 p.c. sulphur dioxide must be present in the entering gas, otherwise too much water is required for the complete condensation of the sulphur dioxide.

The liquid sulphur dioxide sold commercially has frequently a purity of 99·8 p.c.

Uses. Sulphur dioxide is largely employed in the arts and manufactures. Its principal use is in the manufacture of sulphuric acid, enormous quantities of the gas being produced for this purpose, principally from pyrites. The liquid acid was formerly largely used in the paper industry in the manufacture of wood pulp, but has now been superseded to a great extent by sulphur dioxide prepared by roasting pyrites. In this process the fir or pinewood is deprived of the bark, cut up into small pieces, and boiled in large lead-lined boilers with a solution of calcium sulphite in excess of sulphurous acid until all incrusting matter is dissolved, and the cellulose can easily be separated from the residue by washing and beating. Sulphur dioxide is also employed to remove the last traces of chlorine after bleaching the pulp: $SO_2+Cl_2+2H_2O=H_2SO_4+2HCl$. It is also used in the refining of sugar, to decolorise the crude sugar juice; it does not invert the sugar, unless exposed to the air for a long time, and has a slight preservative action. It has been employed in tanning to soften dry hides and skins in the bath or 'soak,' which consists of a solution of sulphur dioxide, and in the 'puring' operation for the purpose of curtailing or dispensing with the use of animal excrement. Sulphur dioxide is a powerful antiseptic and has been successfully employed in preserving meat and stopping fermentation, fumigating clothes, and disinfecting the air of rooms. Instead of burning sulphur for disinfecting purposes, the sulphur dioxide can conveniently be obtained from the liquid oxide.

Sulphur dioxide is used in the extraction of alum from shale in a process worked at Ampsin near Lüttich; in the Hargreaves process for the manufacture of salt cake; as a fire extinguisher; and in the bleaching of wool, silk, feathers, sponges, starch, and many other substances.

The materials to be bleached may be treated either with the gas or the solution, the latter being less effective. The goods, after washing and wringing, are brought, while still damp, into a closed chamber, and covered with a thick cloth. They are then exposed to the action of sulphur dioxide for 12–24 hours according to the whiteness required. They are then washed in lukewarm, dilute hydrochloric acid to remove particles of adhering sulphur deposited on them. For bleaching loose wool a solution of sodium bisulphite is preferably used, the substance being afterwards passed through lukewarm, dilute hydrochloric acid, whereby sulphur dioxide is evolved in the nascent condition and bleaches the wool (Dingl. poly. J. 245, 183).

Sulphurous acid has been used to a considerable extent for the purpose of giving to old barley the fine yellow colour of the new grain. Such treatment is injurious to the germinating power, and may be detected by steeping the barley in hot water for a quarter of an hour, then adding zinc and hydrochloric acid to the aqueous extract, the presence of sulphur being indicated by the evolution of hydrogen sulphide (Eckenroth).

Sulphur dioxide has been employed in the treatment of cutaneous diseases, the patient sitting in a box provided with an aperture at the top, through which his head passes, while a wet cloth around his neck prevents the escape of gas from within. The box is over a small fireplace in which sulphur is burned, so that the patient sits in an atmosphere of sulphur dioxide.

The liquid oxide is employed principally as a source of the gas, but is also used directly to some extent in the manufacture of artificial ice, and the extraction of certain fats and oils.

Sulphurous acid. This acid is known only in solution, which is prepared by saturating water with sulphur dioxide. The resulting liquid smells and tastes of the gas, and has a strongly acid reaction. On preservation for some time in contact with air the smell disappears, oxygen being absorbed, and sulphuric acid formed. The acid is dibasic, and forms two series of salts known as sulphites, the two types $R'HSO_3$ and R''_2SO_3 being termed acid and normal sulphites respectively. The normal sulphites of the alkalis are easily soluble in water, while those of the other metals are almost, or quite, insoluble. These latter dissolve, however, in aqueous sulphurous acid with formation of the acid sulphites, but the solution thus obtained is again decomposed on evaporation with evolution of SO_2, and formation of the normal salt. In addition to the two series of sulphites mentioned above, a third series is known, termed metabisulphites, of the formula $R''_2S_2O_5$. Only the alkali salts of this last class have been prepared.

The normal sulphites have no odour, and those which dissolve in water possess a sharp taste. They are easily detected by the addition of sulphuric acid when they evolve the pungent-smelling SO_2. Their neutral solutions give a white precipitate with barium chloride, which is easily soluble in dilute hydrochloric acid; on adding nitric acid to this solution and warming, a precipitate of barium sulphate is obtained.

The existence of isomeric double sulphites, which are theoretically possible owing to the unsymmetrical formula of sulphurous acid $H{\cdot}SO_2{\cdot}OH$, has been announced by Schwicker (Ber. 22, 1728), who describes two different salts to which he assigns the formulæ $Na{\cdot}SO_2{\cdot}OK$ and $K{\cdot}SO_2{\cdot}ONa$. Subsequent observers have, however, failed to obtain these compounds, and their existence is not satisfactorily established, *see* Godby, Chem. Soc. Proc. 1907, 241; Arbusoff, Chem. Soc. Abstr. 1909, ii. 573.

Sulphur sesquioxide. Buchholz was the first to observe the formation of a blue solution when flowers of sulphur were dissolved in Nordhausen sulphuric acid. Vogel found that the same colour was produced with S and SO_3, but Weber was the first to show that it was due to the formation of a new oxide of sulphur (Pogg. Ann. 1875, 156, 531).

Sulphur sesquioxide is obtained by dissolving flowers of sulphur in an excess of sulphur trioxide cooled to 15°, when it forms bluish-green crusts resembling malachite. It may be isolated by pouring off as much as possible of the excess of SO_3, and distilling off the rest at a temperature of about 38°, the sesquioxide remaining behind. It forms a crystalline, blue-green mass, which easily decomposes, especially on heating, into sulphur and sulphur dioxide. In moist air it absorbs water, giving a brown liquid, which soon decomposes with precipitation of sulphur. It is soluble in fuming sulphuric acid, producing a blue solution, which is comparatively stable, and may be kept for a considerable time in a sealed tube, but eventually decomposes, giving a brown solution with evolution of sulphur dioxide and precipitation of sulphur. This solution is used in the manufacture of certain colours (sulphur colours), such as thiopyronine.

Sulphur trioxide SO_3. Sulphur trioxide was known to the alchemists under the name of 'philosophical salt,' and a method for its preparation by the distillation of ferric sulphate is mentioned by Lemery in 1675. Its relations to oil of vitriol were first recognised by Scheele and Guyton de Morveau in 1786.

Preparation. Sulphur trioxide may be prepared by carefully heating fuming sulphuric acid in a retort, and collecting the distillate in a well-cooled receiver. It is also formed when concentrated sulphuric acid is distilled with an excess of phosphorus pentoxide, and by the dry distillation of many metallic sulphates, especially ferric sulphate. Sulphur dioxide unites directly with oxygen to form sulphur trioxide in the presence of certain substances such as platinised asbestos and ferric oxide, which act as catalysts, and this reaction is now employed on the large scale in the contact process for manufacturing sulphuric acid (*q.v.*). Sulphur trioxide is also produced to some extent when sulphur dioxide is decomposed by heat or by passing electric sparks through it, as well as during the combustion of sulphur and the roasting of metallic sulphides. If pure sulphur trioxide be required, the product obtained by any of the above processes must first be redistilled several times, and finally purified by repeatedly heating it until it has almost entirely melted and then pouring off the liquid from the portions still remaining solid. The sulphur trioxide may be regarded as pure when the whole mass melts easily and completely on gentle warming.

Properties. Sulphur trioxide exists in two modifications termed α and β respectively. The two substances have different physical properties but resemble one another in their chemical behaviour.

α-Sulphur trioxide forms long colourless needles of sp.gr. 1·944 at 11° (Schenck, Annalen, 1901, 316, 1), which melt at 14·8° (Rebs), 16·79° (Lichty), and at temperatures below 25° gradually pass over into the β modification. The liquid boils at 44·88° (Lichty, Amer. Chem. J. 1912, 34, 1440), and its molecular weight corresponds with the formula SO_3 (Oddy, Gazz. chim. ital. 1901, 31, (2), 158).

β-Sulphur trioxide crystallises in colourless needles of sp.gr. 1·97 at 20°, which resemble asbestos in appearance. On heating, it volatilises at about 50° without previous fusion, and is converted into the α modification by distillation. According to Oddy, the molecular weight of the β compound corresponds with the formula S_2O_6 (see, however, Lichty, *l.c.*). The β modification is chemically rather less active than the α modification.

Perfectly dry sulphur trioxide shows no acid reaction and is not corrosive. On heating, it is decomposed into sulphur dioxide and oxygen, but a temperature of 1300° is required for the reaction to be complete. On exposure to air it absorbs moisture rapidly, emitting dense white fumes, whilst it combines with water with explosive violence, producing sulphuric acid. Owing to this avidity for water, sulphur trioxide chars many organic substances.

Sulphur trioxide forms stable compounds with many substances, such as iodine, with which it gives the compounds $I_2(SO_3)_6$ and $I_2(SO_3)_2$. With tellurium it forms $TeSO_3$, a solid possessing a characteristic red colour. Compounds of sulphur trioxide with the oxides of arsenic and nitrogen are also known.

Uses. Sulphur trioxide is manufactured on the large scale for use in the preparation of artificial dyestuffs, in which it is employed as a sulphonating and oxidising agent. It is formed as an intermediate body in the contact process for manufacturing sulphuric acid (*q.v.*).

Hyposulphurous acid (*Hydrosulphurous acid*). Berthollet, in 1789, found that iron dissolved in an aqueous solution of sulphur dioxide without evolution of hydrogen, and Fourcroy and Vauquelin discovered in 1798 that tin and zinc behave similarly. Schönbein studied the reaction between zinc and sulphurous acid, and showed that the solution thus obtained possessed strong reducing properties, and that it contained the salt of a sulphur acid containing less oxygen than sulphurous acid, but the true nature of the reaction was first traced by Schützenberger, to whom the credit of the discovery of hyposulphurous acid is due (Compt. rend. 1869, 69, 196).

Preparation. The zinc salt of the acid is produced when zinc is dissolved in a strong solution of sulphurous acid, and the solution so obtained was mistaken by Schützenberger for the free acid: $Zn+2SO_2=ZnS_2O_4$.

A better method for preparing hyposulphites is that of Bernsthen and Balzen (Ber. 1900, 33, 126). A concentrated solution of sodium bisulphite is shaken with zinc dust, and sulphur dioxide is passed into the liquid

$$2NaHSO_3+SO_2+Zn=Na_2S_2O_4+ZnSO_3+H_2O$$

Milk of lime is then added until the zinc is precipitated, the solution filtered, and the filtrate saturated with sodium chloride. On cooling the liquid, crystals of $Na_2S_2O_4,2H_2O$ separate out.

Sodium hyposulphite is formed in the electrolytic reduction of sodium bisulphite, but it is difficult to prevent the reduction from proceeding further, with the consequent formation of thiosulphate: $Na_2S_2O_4+H_2=Na_2S_2O_3+H_2O$.

By using suitable precautions, solutions containing 30–40 grms. of hyposulphite per litre can be obtained (Frank, Zeitsch. Elektrochem. 1904, 10, 460). If the bisulphite be electrolysed in the presence of indigo, indigo-white is produced, the hyposulphite first formed acting on the indigo, and this process is now employed commercially.

The hyposulphites can also be prepared in a pure condition by means of a reaction discovered by Moissan (Compt. rend. 1902, 135, 647) which consists in passing a current of sulphur dioxide over metallic hydrides

$$K_2H_2+2SO_2=K_2S_2O_4+H_2.$$

The hyposulphites of potassium, sodium, rubidium, caesium, lithium, calcium, and strontium have been obtained in this way.

The free acid is known only in solution; it can be prepared by decomposing a solution of the sodium salt with oxalic acid. A yellow liquid is thus obtained, which soon decomposes, absorbing oxygen from the air with formation of thiosulphuric acid, which itself rapidly splits up into sulphur and sulphur dioxide.

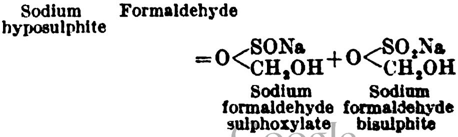
Constitution and properties of hyposulphites. Schützenberger in 1869 obtained a crystalline salt to which he assigned the formula $NaHSO_2$. Bernsthen, from his own work, regarded the sodium salt as $Na_2S_2O_4$, but as neither chemist had succeeded in preparing the salt in a pure condition, and the percentage composition corresponding to the two formulæ is almost the same, the true formula of the hyposulphites remained uncertain until Nabl succeeded in obtaining a pure zinc salt by passing SO_2 into absolute alcohol in presence of zinc turnings, and established the formula $H_2S_2O_4$ for the acid. This was confirmed by Bernsthen and Balzen (Ber. 1900, 33, 126).

The hyposulphites are to be regarded as derived from a mixed anhydride of sulphurous acid and the hypothetical sulphoxylic acid H·SO·OH, the sodium salt being represented by the formula $O{<}\begin{smallmatrix}SO_2Na\\SONa\end{smallmatrix}$. This view of its constitution is borne out by its behaviour towards organic reagents (*see*, however, Bucherer and Schwalbe, Ber. 1906, 39, 2814).

The hyposulphites are strong reducing agents, and on this property their commercial importance depends; both in the solid state when moist, and in aqueous solution, they absorb oxygen rapidly, forming metabisulphites. When added to dilute acid solutions of copper, silver, gold, &c., they precipitate the metal in a colloidal condition; a strong solution of copper sulphate gives a mixture of copper and copper hydride. This latter reaction distinguishes hyposulphurous acid from the other sulphur acids. For the analysis of solutions containing hyposulphites, *see* Orloff, Chem. Soc. Abstr. 1905, ii. 200; Seyewetz and Block, Bull. Soc. chim. 1906, 35, 293.

For the method of preparing pure sodium hyposulphite from the commercial salt, *see* Jellinek, Zeitsch. anorg. Chem. 1911, 71, 96.

Sodium hyposulphite. Sodium hyposulphite is now prepared on the large scale for use as a reducing agent in the dyeing and calico-printing industries. It is usually made by the action of zinc on a solution of sodium bisulphite, and subsequent removal of the zinc by milk of lime, the sodium hyposulphite being precipitated from the filtered solution by the addition of salt, when the compound $Na_2S_2O_4,2H_2O$ is obtained. This salt is unstable, but on treating it with boiling alcohol the water of crystallisation can be removed, and the resulting anhydrous salt is comparatively stable. This latter compound is sold under the name of 'Hydrosulphite BASF,' and contains about 90 p.c. of pure hyposulphite. It is fairly stable in a dry state, but cannot be used in calico-printing as a discharge, as it is oxidised on steaming. This objection was overcome by the discovery of the formaldehyde compounds of sodium hyposulphite, first used at the print-works of Zündel in Moscow. These compounds are obtained by adding a solution of formaldehyde to a solution of sodium hyposulphite. The resulting substance is a mixture in equimolecular proportions of sodium formaldehyde bisulphite and sodium formaldehyde sulphoxylate



$$\underset{\text{Sodium hyposulphite}}{O{<}\begin{smallmatrix}SO_2Na\\SONa\end{smallmatrix}}+\underset{\text{Formaldehyde}}{2CH_2O}+H_2O$$

$$=\underset{\substack{\text{Sodium formaldehyde}\\\text{sulphoxylate}}}{O{<}\begin{smallmatrix}SONa\\CH_2OH\end{smallmatrix}}+\underset{\substack{\text{Sodium formaldehyde}\\\text{bisulphite}}}{O{<}\begin{smallmatrix}SO_2Na\\CH_2OH\end{smallmatrix}}$$

These salts, the mixture of which is sold under the names of Hydrosulphite NF, Rongalite C, &c., are perfectly stable at ordinary temperatures, and are not in themselves reducing agents. On steaming, or boiling with water, they are decomposed into their constituents, and the hyposulphite set free acts as a reducing agent in the usual way. They are employed as discharges for cotton. It was found that by the action of zinc on sodium formaldehyde bisulphite the whole of this could be converted into the sulphoxylate compound which is now manufactured in the above manner, the resulting sodium formaldehyde sulphoxylate being sold as Hydrosulphite NF conc., Hyraldite C extra, &c. It has the formula $NaHSO_2,CH_2O,2H_2O$.

The various commercial brands of hydrosulphite are used as discharges in calico-printing, as stripping agents, and in the dyeing of certain vat colours, such as indigo. Mixtures of the sodium formaldehyde sulphoxylate with small amounts of certain anthraquinone derivatives (which act as catalytic agents), are used for discharging some insoluble azo colours developed on the fibre, *e.g.* α-naphthylamine claret, which resist the action of hydrosulphite alone. Mixtures of the above-named compound with the zinc compounds of some quaternary ammonium bases, such as the zinc compound of dimethylphenylbenzylammonium chloride are used in discharging indigo and other vat dyestuffs, the 'leucotrope' as it is termed, combining with the reduced dyestuff, and preventing its re-oxidation.

Sodium hyposulphite is also employed as a decolouriser for sugar juice, and as an absorbent for oxygen to replace pyrogallol in gas analysis.

Thiosulphuric acid $H_2S_2O_3$. This acid was first prepared in the form of its sodium salt by Chaussier in 1799, who obtained it whilst trying to make sodium carbonate by fusing sodium sulphate with carbon. The acid received at first the name of hyposulphurous acid, the present name, thiosulphuric acid, being proposed by Wagner. The free acid is known only in solution, and even this is very unstable and rapidly decomposes with evolution of sulphur dioxide and precipitation of sulphur. Small quantities of the acid are formed by the action of a solution of sulphurous acid on flowers of sulphur at ordinary temperatures, more rapidly at 80°.

Preparation of thiosulphates. Thiosulphates may be obtained by boiling solutions of the sulphites with flowers of sulphur

$$K_2SO_3+S=K_2S_2O_3.$$

They are also produced, together with polysulphides, by fusing the alkaline carbonates with sulphur, or by boiling the caustic alkalis with water and sulphur

$$6KOH+12S=2K_2S_5+K_2S_2O_3+3H_2O.$$

Alkaline and alkaline earth sulphides, particularly the polysulphides, furnish thiosulphates on oxidation either by the oxygen of the air or by suitable oxidising agents.

When iodine acts on a mixture of equimolecular proportions of sodium sulphide and sulphite, a quantitative yield of thiosulphate is obtained (Spring, Ber. 1874, 7, 1157).

Thiosulphates may also be prepared by the electrolysis of ammoniacal sulphite solutions (Halphen, J. Pharm. Chim. 1894, 29, 371).

Properties. The thiosulphates are mostly soluble in water, and frequently crystallise well. The most important one is the sodium salt commonly known as sodium hyposulphite (*see* under SODIUM).

All the soluble thiosulphates contain water of crystallisation, which cannot usually be completely expelled without the salt undergoing decomposition. On strongly heating they all decompose, leaving a mixture of sulphate and sulphide. The same decomposition takes place when their aqueous solutions are boiled for a considerable time, hydrogen sulphide being evolved, and a sulphate remaining in solution. Their solutions are oxidised by mild oxidising agents, such as iodine, and ferric chloride, to tetrathionates (*q.v.*), and the electrolytic oxidation of neutral or acid thiosulphate solutions yields the same compounds. Powerful oxidising agents, on the other hand, convert the thiosulphates into sulphates, in some cases with intermediate formation of tetrathionates (Longi, Gazz. chim. ital. 1896, 26, 119). Reducing agents convert them into a mixture of sulphite and sulphide. The constitutional formula of thiosulphuric acid being $SO_2<\substack{OH\\SH}$, it might be expected that isomeric thiosulphates, such as $SO_2<\substack{OK\\SNa}$ and $SO_2<\substack{ONa\\SK}$ might exist. According to Schwicker (Ber. 22, 1733), such isomerides have been prepared, but later workers have failed to obtain them, and their existence must at present be regarded as doubtful (*see* Rohrig, J. pr. Chem. [ii.] 37, 250; Barth, Zeitsch. physikal. Chem. 9, 176; Meyer and Eggeling, Ber. 1907, 1351; Gutmann, *ibid.* 1908, 307).

A very large number of double thiosulphates have been prepared and examined, for details as to which the original papers should be consulted (*see* C. and J. Bhaduri, Zeitsch. anorg. Chem. 1898, 17, 1; Rosenheim and Steinhauser, *ibid.* 1900, 25, 72; Meyer and Eggeling, *l.c.*).

Dithionic acid $H_2S_2O_6$. This acid was discovered by Welter and Gay-Lussac in 1819. It may be prepared by passing a current of sulphur dioxide through ferric hydroxide suspended in water at a temperature of 0°. At first a reddish-brown solution of ferric sulphite is obtained, which rapidly changes to pale green, the solution then containing ferrous sulphite and dithionate. Baryta water is then added, and the liquid filtered. The calculated quantity of sulphuric acid necessary to precipitate the barium in solution is added to the filtrate, and the resulting solution evaporated *in vacuô* until it attains a sp.gr. of 1·347. On attempting to concentrate it further, it is resolved into sulphur dioxide and sulphuric acid, and its aqueous solution on exposure to air also oxidises with formation of the latter body.

Instead of ferric hydroxide, manganese dioxide can be employed in the above method of preparing dithionic acid, but the yield is then not so satisfactory. The action of sulphur dioxide on various metallic oxides with production of dithionates has been studied by Carpenter (Chem. Soc. Trans. 1902, 1). Dithionates are also obtained by the addition of hydrogen peroxide to a 33 p.c. solution of sodium thiosulphate, the solution being kept neutral during the addition of the peroxide by the simultaneous addition of an acid, the reaction being represented by the following equation

$$2Na_2S_2O_3+H_2O_2=Na_2S_2O_6+2NaOH.$$

The dithionates are most easily obtained from the barium salt, by double decomposition with the sulphate of the corresponding base. Only the neutral salts are known. They are all soluble in water, and usually crystallise well, all except the potassium salt containing water of crystallisation. Their solutions are not oxidised by atmospheric oxygen in the cold, but on heating a sulphate is produced; nascent hydrogen reduces dithionates to sulphites. On heating the dry salts they decompose, partially at 100°, completely at a higher temperature, evolving sulphur dioxide and leaving a residue of sulphate.

The formation of dithionate by heating silver sulphite or silver-sodium sulphite shows that dithionic acid is composed of two sulphoxyl radicles $(SO_3H)_2$, and has not the formula SO_2,OH assigned to it by Kolbe (Baubigny, Compt. rend. 1910, 150, 973).

Dithionic acid may be separated from the other thionic acids by treatment of the mixture with alkaline permanganate, or sodium hypobromite. A solution of barium acetate is then added, and the barium sulphate filtered off. The filtrate contains the dithionate.

Literature. Welter and Gay-Lussac, Ann. Chim. Phys. 1819, 10, 312; Gélis, *ibid.* 65, 222; Spring and Bourgeouis, Bull. Acad. Roy. 1878, 45, 151; Meyer, Ber. 34, 3606; Hauer, J. pr. Chem. [i.] 80, 229; Péan de Saint-Gilles, Ann. Chim. Phys. [ii.] 55, 374; Buignet, J. Pharm. Chim. 38, 122; Fordos and Gélis, *ibid.* 36, 113; Dymond and Hughes, Chem. Soc. Trans. 71, 314; Jacquelin, Ann. Chim. Phys. [iii.] 21, 110; Rathke and Zschiesche, J. pr. Chem. 92, 141; Otto, Annalen, 147, 187; Kolbe, J. pr. Chem. [i.] 19, 484; Heeren, Pogg. Ann. 7, 191; Carpenter, Chem. Soc. Trans. 1902, 1; Friessner, Zeitsch. Elektrochem. 10, 265.

Trithionic acid $H_2S_3O_6$. This compound was discovered by Langlois in 1842, who obtained the potassium salt by gently heating a solution of potassium bisulphite with sulphur

$$6KHSO_3+S_2=2K_2S_3O_6+K_2S_2O_3+3H_2O.$$

The reaction probably takes place in two stages, in the first of which the thiosulphate is formed, and this is then converted into trithionate by the action of sulphur dioxide. This view is supported by the fact that potassium trithionate can be obtained by acting on the thiosulphate with sulphur dioxide:

$$2K_2S_2O_3+3SO_2=2K_2S_3O_6+S.$$

The sulphur then acts further on the trithionate to form tetra- and pentathionate (Plessy). The free acid may be prepared by adding hydrofluosilicic acid to a solution of the potassium salt, when insoluble potassium silicofluoride is precipitated, and trithionic acid set free. The dilute solution of the acid thus obtained is stable, but on attempting to concentrate it, even *in vacuó*, it decomposes into sulphur, sulphur dioxide, and sulphuric acid

$$H_2S_3O_6=S+SO_2+H_2SO_4.$$

It has no smell, but possesses a strongly bitter taste.

Preparation of trithionates. A convenient way of preparing trithionates consists in acting on a thiosulphate with a persulphate, the former salt being kept in excess, when a good yield of trithionate is obtained (Marshall, J. Soc. Chem. Ind. 1897, 16, 396).

Certain double thiosulphates undergo decomposition when boiled with water, producing trithionates. Colefax has shown (Chem. Soc. Trans. 1892, 181, 1083; 1908, 811) that iodine does not oxidise a mixture of sodium sulphite and thiosulphate directly to trithionate, as was formerly thought to be the case, but that when the iodine is present in insufficient quantity to convert all the sulphite into sulphate, the residual sulphite abstracts sulphur from the tetrathionate (formed by oxidation of the thiosulphate) to produce a trithionate. According to Willstätter (Ber. 1903, 36, 1831) the oxidation of sodium thiosulphate by hydrogen peroxide gives rise to trithionate and sulphate.

Properties. The trithionates are all soluble in water, with the exception of the silver and mercury salts, and frequently crystallise well. Their solutions oxidise on exposure to air, forming sulphates and liberating sulphur and sulphur dioxide, and the same decomposition ensues on heating the solid salts. Sodium amalgam converts the salts into a mixture of sulphite and thiosulphate, whilst sodium arsenite or stannite reduces them completely to sulphites (Gutmann, Ber. 1905, 38, 1728, 3277).

The trithionates of potassium, rubidium, and cæsium have been prepared and crystallographically examined by Mackenzie and Marshall (Chem. Soc. Trans. 1908, 1726). *See* also Plessy, J. pr. Chem. 1844, [i.] 33, 348; Chancel and Diacon, Compt. rend. 1863, 56, 710; Fordos and Gélis, *ibid.* 1843, 16, 1070; Rathke, J. pr. Chem. 1865, [i.] 95, 1; Hertlein, Zeitsch. physikal. Chem. 1896, 19, 287.

Tetrathionic acid $H_2S_4O_6$. This acid was discovered in 1843 by Fordos and Gélis, who also prepared certain of its salts. They obtained it from its barium salt, which is formed when iodine acts on barium thiosulphate suspended in water $2BaS_2O_3+I_2=BaS_4O_6+BaI_2$. The thiosulphate of lead is, however, preferable to that of barium in preparing the acid, since the latter salt gives rise to the simultaneous formation of a little trithionate as well. The lead thiosulphate is suspended in water and iodine carefully added, when soluble lead tetrathionate and insoluble lead iodide are produced. The liquid is filtered, the lead in the filtrate precipitated by the addition of a slight excess of sulphuric acid, and the excess of the latter removed by the cautious addition of baryta water. The solution of the free acid thus obtained may be concentrated by evaporation *in vacuó*. Tetrathionic acid is only known in the form of its aqueous solution; this is colourless, odourless, and strongly acid. On concentration beyond a certain point it decomposes in a similar manner to trithionic acid. Sulphuric acid and hydrochloric acid have no action on it in the cold; on heating, this latter acid disengages sulphuretted hydrogen. Oxidising agents, such as nitric acid, convert tetrathionic acid into sulphuric acid, while reducing agents (sodium amalgam) form thiosulphate.

Preparation. The tetrathionates are formed by the partial oxidation of thiosulphates, a convenient oxidising agent being potassium persulphate (Marshall, J. Soc. Chem. Ind. 1897, 16, 396)

$$K_2S_2O_8+2BaS_2O_3=2BaSO_4+K_2S_4O_6.$$

If an excess of thiosulphate be employed a trithionate is produced (v. *supra*).

The electrolytic oxidation of thiosulphates in neutral or acid solution also gives rise to tetrathionates, the oxidation under these conditions not proceeding further (Thatcher, Zeitsch. physikal. Chem. 1904, 47, 641).

Properties. The tetrathionates are all soluble in water; their solutions oxidise on exposure to air, forming sulphate, pentathionate, and other products. On boiling the solution, the products are sulphur dioxide, sulphur, and a sulphate (Gutmann, Ber. 1908, 41, 300).

The dry salts decompose on heating into mixtures of dithionates and trithionates, or, in the case of the tetrathionates of the heavy metals, into sulphide and sulphate.

Pentathionic acid $H_2S_5O_6$. This acid was discovered by Wackenroder in 1846. It is obtained by passing a slow current of sulphuretted hydrogen into water which has been previously almost saturated with sulphur dioxide, allowing the liquid to stand for some time, then again passing in sulphur dioxide, and repeating this cycle of operations several times. The liquid so obtained contains in addition to pentathionic acid, free sulphur, both in solution and in suspension, sulphuric acid, thiosulphuric acid, and small amounts of tri- and tetrathionic acids, possibly also hexathionic acid. The liquid is filtered as far as possible from the sulphur, and a little freshly-precipitated barium carbonate added, which precipitates the sulphuric acid formed, together with the remainder of the sulphur, which is removed along with the barium sulphate by filtration. The clear filtrate is concentrated on a water-bath until it attains a sp.gr. of 1·32, and the concentration is then continued *in vacuô* at the ordinary temperature to a sp.gr. of 1·46, when the residual liquid consists mainly of pentathionic acid (Wackenroder, Ann. Chim. Phys. 1846, 60, 189; Kessler, Pogg. Ann. 74, 249; Takatmatsu and Smith, Chem. News, 1880, 41, 290; Lewes, Chem. Soc. Trans. 39, 68; 41, 300). On attempting to concentrate it further, or on heating its solution, the acid decomposes into sulphuric acid, sulphur dioxide, sulphuretted hydrogen, and sulphur. On adding, with constant stirring, to the concentrated solution of the acid about half the quantity of caustic potash required for complete neutralisation, and filtering from any precipitated sulphur, the clear liquid gives on spontaneous evaporation well-defined crystals of potassium pentathionate $K_2S_5O_6,H_2O$ (Lewes). This salt can be recrystallised from solutions at 50° containing a little free sulphuric acid, but it is at once decomposed in the presence of alkalis. A better method of obtaining the salt consists in adding potassium acetate instead of caustic potash to the concentrated solution of the acid. The potassium salt dissolves in about twice its weight of water to form a clear neutral solution, which decomposes on standing, more quickly on heating, forming a tetrathionate and free sulphur. The dry salt, if freed from water by washing with alcohol, is much more stable, and can be kept unaltered for a long time. On heating the salt it evolves sulphur dioxide and sulphur, and leaves a sulphate:

$$2K_2S_5O_6=2K_2SO_4+2SO_2+3S_2.$$

Oxidising agents convert pentathionates into sulphates. Caustic soda decomposes pentathionates, the action varying with the conditions. With dilute alkali a tetrathionate and sulphur are produced in the cold; sulphur and a trithionate on heating. With an excess of alkali a thiosulphate and sulphite are formed, or on heating to boiling, thiosulphate alone

1. $2K_2S_5O_6+6KOH=2K_2SO_3+3K_2S_2O_3+S_2+3H_2O$
2. $2K_2S_5O_6+6KOH=5K_2S_2O_3+3H_2O.$

Sodium amalgam converts pentathionates into thiosulphates; or on continued action, into sulphides.

Pentathionic acid is also produced by the action of hydriodic acid and iodine, or sulphuretted hydrogen, on lead thiosulphate (Persoz; Takatmatsu and Smith).

The pentathionates have been little examined; the copper salt $CuS_5O_6,4H_2O$ forms small blue crystals, easily soluble in water (Debus).

Hexathionic acid $H_2S_6O_6$. The possible existence of the potassium salt of this acid in the mother liquor of Wackenroder's solution has been indicated by Debus (Chem. Soc. Trans. 1888, 53, 278), but neither the acid nor any of its salts have been prepared in a pure condition. The potassium salt is said to form a warty, non-crystalline mass, which readily decomposes in solution, even in the presence of dilute sulphuric acid.

Takamatsu and Smith (*ibid.* 37, 608) give a table (p. 310) of reactions to distinguish tetra- and pentathionic acids from each other, and from the other thionic acids.

Literature. Plessy, Compt. rend. 21, 473; Ann. Chim. Phys. [iii.] 20, 162; Thomson, Ann. Phil. 12, 441; Lenoir, Annalen, 62, 253; Ludwig, Arch. Pharm. 51, 259; Fordos and Gélis, Ann. Chim. Phys. [iii.] 22, 66; 28, 451; Rister-Bennet, Pogg. Ann. [ii.] 116, 470; Chancel and Diacon, Compt. rend. 56, 710; Rammelsberg, J. 10, 136; W. Spring, Ber. 6, 1, 108; Annalen, 199, 97; 213, 329; Stingl and Morawski, J. 1879, 1110; Curtius, J. pr. Chem. [ii.] 27, 24, 225; Shaw, Chem. Soc. Trans. 43, 351; Smith, *ibid.* 43, 355; Salzer, Ber. 1886, 1696; Kessler, Pogg. Ann. [ii.] 74, 294; Takamatsu and Smith, Chem. Soc. Trans. 1880, 37, 592; Lewes, *ibid.* 1882, 300; Shaw, *ibid.* 1883, 351; Valeton, Chem. Soc. Abstr. 1907, ii. 811.

Sulphur heptoxide S_2O_7. This oxide of sulphur was discovered by Berthelot, who obtained it by submitting a mixture of equal volumes of SO_2 and O to the silent electric discharge. It forms a viscid liquid, which becomes solid at 0°, forming white, crystalline needles. It is very volatile, and decomposes slowly at the ordinary temperature, rapidly on heating, into sulphur trioxide and oxygen, but may be kept unchanged for some time at a low temperature. Water decomposes it with formation of sulphuric acid and oxygen.

Persulphuric acid. A solution of this acid is obtained by the electrolysis of dilute sulphuric acid, and its formation was observed by Berthelot, although he did not isolate it. It is best prepared by the electrolysis of an acid of sp.gr. 1·35–1·50, the current density being 500 ampères per square decimetre (Elbs and Schönherr, Zeitsch. Elektrotech. and Elektrochem. 1895, 245, 468). It slowly undergoes decomposition in solution into sulphuric acid and Caro's acid,

Reagents	Dithionic acid $H_2S_2O_6$	Trithionic acid $H_2S_3O_6$	Tetrathionic acid $H_2S_4O_6$	Pentathionic acid $H_2S_5O_6$
Caustic potash .	No ppt.	No ppt.	No ppt.	Immediate ppt. of sulphur
Dilute hydrochloric acid	No action	Evolution of SO_2, and ppt. of S	No action	No action
Mercurous nitrate	No ppt.	Immediate black ppt., turning white on standing	Yellow ppt., gradually darkening	Yellow ppt. at first, turning white with excess of reagent on standing
Silver nitrate	No ppt.	Yellow ppt., soon turning black	Yellow ppt., soon turning black; also blackened on adding ammonia	Yellow ppt., gradually darkening; black on adding ammonia
Ammoniacal silver nitrate	—	No brown colour, even on standing. On warming, Ag_2S formed	No brown colour, even on standing, unless warmed	Almost immediate brown coloration, turning black on warming
Mercuric cyanide	No ppt.	—	At first, yellow ppt.; turns black on warming, with evolution of HCN	At first, yellow ppt.; gradually turns black on warming with evolution of HCN
Mercuric chloride	No ppt.	Yellow ppt., turning white with excess of reagent	White ppt. on warming	Whitish-yellow ppt. on warming
Potassium hydrosulphide	—	—	White ppt. of sulphur	White ppt. of sulphur
Dilute potassium permanganate solution	One drop, immediate brown ppt.	One drop, immediate brown ppt., even in presence of dilute H_2SO_4	Decolorised, without addition of dilute H_2SO_4. No ppt.	Decolorised, without addition of dilute H_2SO_4. No ppt.

which itself slowly breaks up into hydrogen peroxide and sulphuric acid

1. $H_2S_2O_8+H_2O=H_2SO_5+H_2SO_4$
2. $H_2SO_5+H_2O=H_2SO_4+H_2O_2$

A solution of the acid can also be obtained by decomposing barium persulphate with the theoretical quantity of dilute sulphuric acid.

Persulphuric acid is obtained in an almost pure condition by the action of 100 p.c. hydrogen peroxide on well-cooled chlorsulphonic acid (*see* under *Caro's acid*). It forms a white, crystalline mass, melting with decomposition at a little above 60°. At the ordinary temperature it is stable and can be kept for months.

Persulphuric acid is formed during the working of accumulators (Robertson, Proc. Roy. Soc. 1892, 105).

Persulphates. The persulphates were first prepared in 1898 by Hugh Marshall, who discovered that crystals of the potassium salt were formed at the anode during the electrolysis of a solution of the sulphates of potassium and cobalt in a 'divided cell'; and also by the electrolysis of a saturated solution of potassium bisulphate in the same apparatus. The ammonium salt was prepared by replacing the $KHSO_4$ by ammonium sulphate and dilute sulphuric acid. By treating a saturated solution of the ammonium salt with barium hydroxide Marshall obtained the barium salt, the excess of baryta being removed by a current of carbon dioxide. The lead salt was obtained by decomposing a solution of the barium salt with sulphuric acid and neutralising the liquid with lead carbonate. By acting on the barium salt with zin sulphate a solution of the zinc salt was obtained

The persulphates are now manufactured o the large scale for use as oxidising agents. Th potassium salt is prepared, as stated above, b electrolysing a solution of potassium bisulphat in a divided cell. If the anode potential be raise by the addition of hydrofluoric acid to the liqui the yield of persulphate is greatly increase and the diaphragm can be dispensed with. current density of 5 ampères per square c gives a good yield of persulphate. Ammoniu persulphate is prepared in a similar manner b electrolysing a solution of ammonium sulphat in dilute sulphuric acid (1 : 7) in a divided ce the inner compartment containing the anod and the ammonium salt, the outer cell th kathode, and dilute acid alone. In the prepar tion of persulphates by electrolysis, the yiel gradually falls off, owing to the formation Caro's acid; the essential conditions for obtain ing a satisfactory yield are, that the curren density at the anode should be high, the anod itself small, and that the solution should be ke cool (*see* Elbs and Schonherr, *l.c.*).

Lithium persulphate cannot be obtained i this manner, since although the salt is formed i cannot be isolated from the solution (Otin Zeitsch. Elektrochem. 1911, 919).

The persulphates are all soluble in water, th least soluble being the potassium salt, whic requires about 56 parts of water at 0° for solu tion. Their solutions slowly decompose o standing with evolution of oxygen and formatio of a sulphate and free sulphuric acid, and th same change takes place rapidly on boiling the liquid. The dry salts decompose on heating according to the following equation

$$2K_2S_2O_8=2K_2SO_4+2SO_3+O_2.$$

The molecular formula of the persulphates has been found from electrical conductivity measurements to be $R_2S_2O_8$ and not RSO_4 (Löwenherz, Chem. Zeit. 16, 838).

Solutions of the persulphates give no precipitate with barium chloride; on warming, however, barium sulphate slowly separates out, and oxygen is evolved. An alkaline lead solution gives a precipitate of the peroxide on boiling. Fehling's solution gives a red precipitate of cuprous oxide. Ferrous sulphate is rapidly oxidised to ferric sulphate, with rise of temperature. Solutions of manganous, nickel and cobalt salts all yield precipitates of the higher oxides when mixed with a persulphate and warmed, and chromium compounds are oxidised to chromates. Persulphuric acid oxidises many organic bodies, converting alcohol into aldehyde, and aniline into a brown colouring matter, and bleaching indigo, litmus, and turmeric solutions. Paper and cloth become quite rotten after being dipped in a solution of a persulphate. Silver nitrate gives, with potassium persulphate, a black precipitate of silver peroxide

$$2AgNO_3+K_2S_2O_8+2H_2O \\ =2KHSO_4+2HNO_3+Ag_2O_2.$$

If, however, a strong solution of ammonium persulphate is treated with ammonia and a small amount of silver nitrate, a vigorous evolution of nitrogen takes place, and the liquid becomes heated to boiling. Silver peroxide is first formed, and this oxidises the ammonia to water, setting free nitrogen. .

By warming a persulphate with concentrated sulphuric acid the oxygen is liberated largely in the form of ozone. With hydrochloric acid chlorine is evolved.

Persulphuric acid may be distinguished from hydrogen peroxide on the one hand, and Caro's acid on the other, by its neither giving a reddish-brown coloration with a solution of a titanium salt, nor reducing a dilute solution of potassium permanganate, whilst it does not immediately liberate iodine from an acidified solution of potassium iodide.

Commercial ammonium persulphate may be purified by making a saturated solution of the salt at 90°, adding ammonia to neutralise the free acid present (due to the partial decomposition of the persulphate), filtering, allowing to cool to 30°, and then adding twice the bulk of alcohol and cooling with ice applied externally. The crystals which separate out are well drained and washed with alcohol and ether, and allowed to dry in the air.

The potassium salt has been employed in photography to remove the last traces of the sodium thiosulphate from negatives after fixing.

Literature. Berthelot, Compt. rend. 86, 20, 71, and 277; 112, 1418; Traube, Ber. 22, 1518; 24, 1764; Mendeleeff, Bull. Soc. chim. [iii.] 38, 168; Marshall, Chem. Soc. Trans. 1891, 771; Richarz, Ber. 21, 1670; Bredig, Zeitsch. physikal. Chem. 1893, 12, 230; Moeller, *ibid.* 1893, 12, 255; Schoop, Zeitsch. Elektrochem. 1895, 273; Lowry and West, Chem. Soc. Trans. 1900, 77, 950; Armstrong and Lowry, Chem. News, 1902, 85, 193.

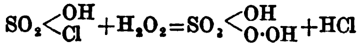
Monopersulphuric acid or **Caro's acid** H_2SO_5. This acid was discovered by Caro in 1898, whilst studying the action of sulphuric acid on persulphates, and was more fully investigated by Baeyer and Villiger (Ber. 1901, 34, 853).

A solution of the acid can be obtained by triturating 10 grms. of potassium persulphate with 20 grms. of concentrated sulphuric acid, allowing the mixture to stand for an hour, pouring it on to ice, and removing the sulphuric acid from the resulting solution by the addition of barium phosphate. The solution thus prepared, containing free phosphoric acid, is tolerably stable, and only very slowly undergoes hydrolysis into hydrogen peroxide and sulphuric acid.

Monopersulphuric acid is also formed during the electrolysis of moderately concentrated sulphuric acid; if an acid of sp.gr. 1·4 be electrolysed, persulphuric acid is first produced, and this is then decomposed by the water present

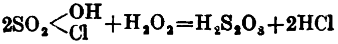
$$H_2S_2O_8+H_2O=H_2SO_5+H_2SO_4.$$

The acid has been prepared in a nearly pure state by D'Ans and Friedrich (Ber. 1910, 43, 1880) by the subjoined method. The calculated amount of 100 p.c. hydrogen peroxide is added to well-cooled chlorsulphonic acid, when an evolution of hydrochloric acid gas takes place. The mixture is allowed to become warm, and the dissolved hydrochloric acid sucked off at the pump. The residue then solidifies to a colourless, crystalline mass, melting at about 45° with slight decomposition. The acid thus prepared has a purity of about 98 p.c. The following equation represents the reaction taking place—



$$SO_2{<}\begin{matrix}OH\\Cl\end{matrix}+H_2O_2=SO_2{<}\begin{matrix}OH\\O{\cdot}OH\end{matrix}+HCl$$

By using twice the quantity of chlorsulphonic acid persulphuric acid is produced (*v. supra*)—



$$2SO_2{<}\begin{matrix}OH\\Cl\end{matrix}+H_2O_2=H_2S_2O_8+2HCl$$

Properties. Monopersulphuric acid is slowly decomposed in aqueous solution with production of hydrogen peroxide and sulphuric acid

$$H_2SO_5+H_2O=H_2SO_4+H_2O_2.$$

This reaction is, however, a balanced one, as a mixture of hydrogen peroxide and concentrated sulphuric acid forms some Caro's acid. It may be distinguished from hydrogen peroxide by its not giving the reddish-brown coloration with titanium salts, and from persulphuric acid by its causing an *immediate* liberation of iodine from an acidified solution of potassium iodide; further, monopersulphuric acid converts aniline into nitrosobenzene, whereas persulphuric acid under similar conditions only produces a brown colouring matter. This reaction takes place more easily with *p*- substituted anilines, such as *p*-bromaniline, than with aniline itself (Morgan).

A mixture of monopersulphuric acid and potassium permanganate forms one of the most powerful oxidising solutions known.

No salts corresponding to this acid have as yet been obtained.

The formula assigned to Caro's acid by Baeyer and Villiger was H_2SO_5. Other chemists (Armstrong and Lowry, Chem. News, 1902, 85, 193; Lowry and West, Chem. Soc. Trans. 1900, 950) regarded it as $H_2S_2O_9$ or $H_2S_4O_{14}$ ($H_2O_2,4SO_3$). The formula H_2SO_5 has been established by Slater Price (Ber. 1902, 291) and D'Ans and Friedrich (*ibid.* 1910, 880).

According to Armstrong and Robertson (Proc. Roy. Soc. 1892, 50, 105) a series of persulphuric acids exist. The acid $H_2O_2,4SO_3$ is supposed to be formed in the presence of strong sulphuric acid and by dilution, acids of the type $H_2O_2,3SO_3$, $H_2O_2,2SO_3$, &c., are successively obtained.

If a persulphate in the state of powder be treated with 100 p.c. sulphuric acid in the cold, a mass possessing a strong odour, recalling that of chloride of lime, is produced. This substance has quite different properties from Caro's acid; thus it reduces potassium permanganate and gives a reddish-brown coloration with titanium salts. The composition of this body has not been definitely established, but according to Baeyer and Villiger its behaviour is possibly due to the presence of a higher oxide of sulphur of the formula S_2O_8.

A method to determine hydrogen peroxide, persulphuric acid, and monopersulphuric acid, when all three are present in solution, has been devised by Baeyer and Villiger (*l.c.*). The amount of monopersulphuric acid present is first determined by adding an acidified solution of potassium iodide, and immediately titrating the liberated iodine with sodium thiosulphate and starch paste. The solution thus decolorised slowly turns blue again on standing, and after 12–24 hours it is again titrated, the iodine now representing the amount of persulphuric acid present. In another portion the hydrogen peroxide is estimated by titration with potassium permanganate. Though not strictly accurate, the method yields satisfactory results.

SULPHURIC ACID. Sulphur trioxide, or sulphuric anhydride, the substance indicated by the formula SO_3, and consisting of 40 parts of sulphur and 60 parts oxygen, combines with water energetically to form a series of products capable of representation by the formula mSO_3nH_2O. Some of these hydrates in which m and n have certain simple integral values are usually recognised as distinct compounds, either on account of certain well-marked physical properties or because of the existence of definite metallic salts derived from them by replacement of the hydrogen by metals, whilst others are considered to be mixtures of these hydrates, or solutions of one or other of them in excess of water.

Starting from **sulphur trioxide** SO_3, which is a crystalline solid, melting at 14·8°, when quite pure and free from water, the more generally accepted compounds are—

Pyrosulphuric acid $2SO_3,H_2O$. A crystalline solid melting at 35°, the melting-point being lowered on the addition of SO_3 or H_2O. Pyrosulphuric acid forms definite crystalline salts, known as the pyrosulphates.

Sulphuric acid SO_3,H_2O. A liquid at the ordinary temperature, but solidifying at about 10·5°, and also forming a large number of well-defined salts, the neutral and acid sulphates.

Dihydrated sulphuric acid $SO_3,2H_2O$. A liquid forming crystals at low temperatures which melt at 8°. Basic lead sulphate Pb_2SO_5 is a salt corresponding to this acid.

Trihydrated sulphuric acid $SO_3,3H_2O$, the hydrate in the formation of which the maximum amount of contraction takes place, and which is represented by the salt, mercury orthosulphate (Turpeth mineral) Hg_3SO_6.

The existence of numerous hydrates in addition to those above-mentioned has been inferred by Pickering (Chem. Soc. Trans. 1890, 648, 331) from the study of various physical phenomena connected with acids of different strengths. One of these $SO_3,5H_2O$ has been isolated in hard, well-defined crystals melting at −25°, whereas mixtures containing either more or less water (within certain limits) melt at lower temperatures.

PHYSICAL PROPERTIES OF SULPHURIC ACIDS.

Commercially, sulphuric acids may be divided into two classes, viz. 'fuming acids' or substances indicated by the formula $m\cdot SO_3\cdot nH_2O$ where $m>n$; and 'non-fuming acids' where $m<n$ varying from O.V. (oil of vitriol), where m very nearly equals n, down to 'chamber acids' of sp.gr. 1·5 and less. The weaker acids on heating lose water, becoming more and more concentrated until finally a product is obtained boiling and distilling at above 300°, and containing between 98 and 99 p.c. H_2SO_4, the remainder being water. Monohydrated acid 100 p.c. H_2SO_4 cannot be obtained in this way, but is readily formed by the addition of the appropriate amount of sulphur trioxide; the monohydrated acid cannot be distilled unchanged, as, on heating, the boiling-point rises from 290° to 338°, a mixture of H_2SO_4,SO_3 and water passing over. It may also be obtained from 98 p.c. acid by cooling it to below 0°, and separating the crystals which form about that temperature, melting them and recrystallising. At ordinary temperatures it is a colourless oily liquid. Its sp.gr. is 1·8385 at 15° (Lunge and Naef), and the addition of a little SO_3 or water raises the sp.gr. It fumes slightly in air, even at ordinary temperatures giving off SO_3, and it is completely dissociated into SO_3 and H_2O at about 440° (Deville and Troost).

NON-FUMING OR ORDINARY SULPHURIC ACIDS.

The following table of the freezing- and melting- and boiling-points is compiled from the results obtained by Lunge (Ber. 1878, 370; and 1881, 2649; Technical Chemists' Handbook, 132).

Per cent. H_2SO_4	Sp.gr.	Boiling-point	Freezing-point	Melting-point
5	1·031	101°	—	—
10	1·069	102	—	—
15	1·107	103·5	—	—
20	1·147	105	—	—
25	1·184	106·5	—	—
30	1·224	108	—	—
35	1·265	110	—	—
40	1·307	114	—	—
45	1·352	118·5	—	—
50	1·399	124	—	—

Per cent. H_2SO_4	Sp.gr.	Boiling-point	Freezing-point	Melting-point
53	1·428	128·5	—	—
56	1·459	133	—	—
60	1·503	141·5	—	—
62·5	1·530	147	—	—
65	1·557	153·5	—	—
67·5	1·585	161	—	—
70	1·615	170	—	—
72	1·639	174·5	—	—
74	1·661	180·5	Liquid at −20°	—
76	1·688	189	Do.	—
78	1·710	199	Do.	—
79·5	1·727	—	−7·5	−7·5
80	1·733	207	−8·5	−8·5
81·3	1·749	—	−0·2	+4·5
82	1·758	218·5	—	—
83·2	1·767	—	+1·6	+6·5
84	1·773	227	+8·5	+8·5
86	1·791	238·5	+4·5	+8·0
88	1·807	251·5	−9·0	−6·0
90	1·818	262·5	—	—
91	1·824	268	Liquid at −20	—
92	1·830	274·5	—	—
93	1·834	281·5	—	—
94	1·837	288·5	—	—
95	1·840	295	Liquid at −20	—

Pictet (Compt. rend. 1894, 119, 642) gives a more complete table of freezing-points, and Knietsch (Ber. 34, 4069), in his tables of the properties of sulphuric acid, gives a still more extended list.

Pictet's Table.

Formula	H_2SO_4 per cent.	Sp.gr.	Fr.pt.
H_2SO_4 . .	100·00	1842	+10°C.
$H_2SO_4+H_2O$.	84·48	1777	+3°C.
„ $+2H_2O$.	73·08	1650	−70°C.
„ $4H_2O$.	57·65	1476	−40°C.
„ $6H_2O$.	47·57	1376	−50°C.
„ $8H_2O$.	40·50	1311	−65°C.
„ $10H_2O$.	35·25	1268	−88°C.
„ $11H_2O$.	33·11	1249	−75°C.
„ $12H_2O$.	31·21	1233	−55°C.
„ $13H_2O$.	29·52	1219	−45°C.
„ $14H_2O$.	28·00	1207	−40°C.
„ $15H_2O$.	26·63	1196	−34°C.
„ $16H_2O$.	25·39	1187	−26·5°C.
„ $18H_2O$.	23·22	1170	−19°C.
„ $20H_2O$.	21·40	1157	−17°C.
„ $25H_2O$.	17·88	1129	−8·5°C.
„ $50H_2O$.	9·82	1067	−3·5°C.
„ $75H_2O$.	6·77	1045	−0°C.
„ $100H_2O$.	5·16	1032	+2·5°C.
„ $300H_2O$.	1·78	1007	+4·5°C.
„ $1000H_2O$.	0·54	1001	+0·5°C.

The specific gravity of dilute sulphuric acid of various degrees of concentration and at various temperatures has been examined by a number of chemists and physicists with results not always exhibiting as close concordance as might be desired; the earlier tables given by Vauquelin, d'Arcet, Ure, Parkes, &c., have long been regarded as superseded by the more exact ones of Bineau and Kolb; and these have been further corrected as a result of the investigations of Lunge, Isler, and Naef. Ure's table, although incorrect, is still largely used as a standard for commercial purposes. For acids approaching the concentration of O.V. the sp.gr. is a fallacious test of strength, because acid of strength 98 p.c. H_2SO_4 has a maximum density as compared with either stronger or weaker acid.

Knietsch's Table.

P.c. SO_3	Melting-point	P.c. SO_3	Melting-point
1	−0·6°C.	65	−4·2°C.
3	−1·7	66	+1·2
5	−2·7	67	+8·0
7	−4·4	68	+8·0
9	−6·0	69	+7·0
11	−7·2	70	+4·0
13	−8·2	71	−1·0
15	−9·3	72	−7·2
17	−11·4	73	−16·2
19	−15·2	74	−25
21	−22·5	75	−34
23	−40·1	76	−32
—	below −40	77	−28·2
61	−40	78	−16·5
62	−20	79	−5·2
63	−11·5	80	+3
64	−4·8	80·63	+10

Apart from this, the effect of temperature variation in altering the sp.gr. is greater, whilst the effect of a given increment in strength is less, the stronger the acid. The table on p. 314 is taken from Lunge's Technical Chemist's Handbook,[1] and is based on the latest results of the above-mentioned investigators with some corrections introduced by the Imperial German Standards Commission.

S. U. Pickering has published (Chem. Soc. Trans. 1890, 64) a number of observations on the sp.gr. of sulphuric acid of strengths between 0·997007 and 99·85700 p.c. of H_2SO_4, in which it is claimed that the limit of error does not, as a rule, exceed 0·000008 (eight parts in one million), notwithstanding that the eight determinations of the strength of the strong sulphuric acid used to prepare other strengths by dilution varied between 99·704 and 99·962 p.c., showing a range of 0·258, or about 1 part in 400. Founded on these results, H. D. Richmond has calculated a table (J. Soc. Chem. Ind. 1890, 479) of specific gravities of sulphuric acid between the limits 1·8248 and 1·8384 referred to water at 15° (90·86–100 p.c.).

Another table, 'the result of a careful selection of figures from standard authorities,' has been calculated by A. H. Elliott (The Chemical Trade Journal, March 24, 1888, 182). W. C. Ferguson (J. Soc. Chem. Ind. 1905, 781) gave the table adopted by the Manufacturing Chemists Association of the United States.

The specific gravity of commercial sulphuric acid, as compared with its strength, usually differs slightly from that found in the case of chemically pure acid, owing to the presence of lead sulphate and other impurities.

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[1] The latest edition of what was previously known as the Alkali-Makers' Handbook.

Specific Gravity of Sulphuric Acid.

At 60°F.=15·5°C.		100 parts by weight contain		1 litre contains kilos. of H_2SO_4	At 60°F.=15·5°C.		100 parts by weight contain		1 litre contains kilos. of H_2SO_4
Sp.gr.	Degrees Twaddell	SO_3	H_2SO_4		Sp.gr.	Degrees Twaddell	SO_3	H_2SO_4	
1·20	40	22·30	27·32	0·328	1·67	134	60·95	74·66	1·246
1·21	42	23·33	28·58	0·346	1·68	136	61·63	75·50	1·268
1·22	44	24·36	29·84	0·364	1·69	138	62·29	76·30	1·289
1·23	46	25·39	31·11	0·382	1·70	140	63·00	77·17	1·312
1·24	48	26·35	32·28	0·400	1·72	142	63·70	78·04	1·334
1·25	50	27·29	33·43	0·418	1·72	144	64·43	78·92	1·357
1·26	52	28·22	34·57	0·435	1·73	146	65·14	79·80	1·381
1·27	54	29·15	35·71	0·454	1·74	148	65·86	80·68	1·404
1·28	56	30·10	36·87	0·472	1·75	150	66·58	81·56	1·427
1·29	58	31·04	38·03	0·490	1·76	152	67·30	82·44	1·451
1·30	60	31·99	39·19	0·510	1·77	154	68·17	83·41	1·478
1·31	62	32·94	40·35	0·529	1·78	156	68·98	84·50	1·504
1·32	64	33·88	41·50	0·548	1·79	158	69·96	85·70	1·534
1·33	66	34·80	42·66	0·567	1·80	160	70·96	86·92	1·565
1·34	68	35·71	43·74	0·586	1·805	161	71·50	87·60	1·581
1·35	70	36·58	44·82	0·605	1·81	162	72·08	88·30	1·598
1·36	72	37·45	45·88	0·624	1·815	163	72·69	89·05	1·621
1·37	74	38·32	46·94	0·643	1·820	164	73·51	90·05	1·639
1·38	76	39·18	48·00	0·662	1·821		73·63	90·20	1·643
1·39	78	40·05	49·06	0·682	1·822		73·80	90·40	1·647
1·40	80	40·91	50·11	0·702	1·823		73·96	90·60	1·651
1·41	82	41·76	51·15	0·721	1·824		74·12	90·80	1·656
1·42	84	42·57	52·15	0·740	1·825	165	74·29	91·00	1·661
1·43	86	43·36	53·11	0·759	1·826		74·49	91·25	1·666
1·44	88	44·14	54·07	0·779	1·827		74·69	91·50	1·671
1·45	90	44·92	55·03	0·798	1·828		74·86	91·70	1·676
1·46	92	45·69	55·97	0·817	1·829		75·03	91·90	1·681
1·47	94	46·45	56·90	0·837	1·830	166	75·19	92·10	1·685
1·48	96	47·21	57·83	0·856	1·831		75·46	92·43	1·692
1·49	98	47·95	58·74	0·876	1·832		75·69	92·70	1·698
1·50	100	48·73	59·70	0·896	1·833		75·89	92·97	1·704
1·51	102	49·51	60·65	0·916	1·834		76·12	93·25	1·710
1·52	104	50·28	61·59	0·936	1·835	167	76·35	93·56	1·717
1·53	106	51·04	62·53	0·957	1·836		76·57	93·80	1·722
1·54	108	51·78	63·43	0·977	1·837		76·90	94·20	1·730
1·55	110	52·46	64·26	0·996	1·838		77·23	94·60	1·739
1·56	112	53·22	65·20	1·017	1·839		77·55	95·00	1·748
1·57	114	53·95	66·09	1·038	1·840	168	78·04	95·60	1·759
1·58	116	54·65	66·95	1·058	1·8405		78·33	95·95	1·765
1·59	118	55·37	67·83	1·078	1·8410		78·69	96·30	1·784
1·60	120	56·09	68·70	1·099	1·8415		79·47	97·35	1·792
1·61	122	56·79	69·06	1·120	1·8410		80·16	98·20	1·808
1·62	124	57·49	70·42	1·141	1·8405		80·43	98·52	1·814
1·63	126	58·18	71·27	1·162	1·8400		80·59	98·72	1·816
1·64	128	58·88	72·12	1·182	1·8395		80·63	98·77	1·817
1·65	130	59·57	72·96	1·204	1·8390		80·93	99·12	1·823
1·66	132	60·26	73·81	1·225	1·8385		81·08	99·31	1·826

Variation of Specific Gravity with Temperature.

0°	10°	20°	30°	40°	50°	75°	100°
1·857	1·846	1·835	1·825	1·816	1·806	1·782	1·762
1·807	1·796	1·784	1·773	1·762	1·751	1·725	1·700
1·754	1·745	1·735	1·726	1·716	1·706	1·683	1·660
1·704	1·695	1·685	1·676	1·666	1·656	1·634	1·610
1·654	1·645	1·635	1·626	1·617	1·608	1·586	1·565
1·604	1·595	1·585	1·576	1·567	1·558	1·537	1·516
1·552	1·544	1·536	1·528	1·520	1·512	1·491	1·469
1·502	1·494	1·486	1·478	1·470	1·462	1·441	1·419
1·452	1·444	1·436	1·429	1·423	1·416	1·395	1·374
1·402	1·394	1·386	1·379	1·372	1·364	—	—
1·352	1·344	1·336	1·330	1·324	1·316	—	—
1·300	1·293	1·287	1·280	1·274	1·267	—	—
1·250	1·243	1·237	1·230	1·224	1·217	—	—
1·200	1·193	1·186	1·180	1·173	1·165	—	—
1·149	1·143	1·137	1·131	1·125	1·119	—	—
1·098	1·093	1·087	1·082	1·077	1·072	—	—
1·048	1·043	1·037	1·032	1·028	1·022	—	—

SPECIFIC HEAT OF SULPHURIC ACID.

Specific gravity	Degrees Baumé	Specific heat	Specific gravity	Degrees Baumé	Specific heat
1·842	66	0·3315	1·320	35	0·67
1·774	63	0·38	1·263	30	0·73
1·711	60	0·41	1·210	25	0·78
1·615	55	0·45	1·162	20	0·82
1·530	50	0·49	1·116	15	0·87
1·453	45	0·55	1·075	10	0·90
1·383	40	0·60	1·037	5	0·95

Specific heat of dilute sulphuric acid. F. Bode gives the foregoing table indicating the relationship between the sp.gr. at 15°, and the specific heat of sulphuric acid (Zeitsch. angew. Chem. 1889, 244; also J. Soc. Chem. Ind. 1889, 543).

A number of determinations of the heat capacity of sulphuric acid solutions of different strengths have also been recorded by S. U. Pickering (Chem. Soc. Trans. 1890, 64).

Tension of aqueous vapour emitted by dilute sulphuric acid. E. Sorel has made a number of experiments, leading to the following results, abridged from much fuller tables (Bull. Soc. Ind. Mulhouse, 1890, 240; also J. Soc. Chem. Ind. 1890, 175). The figures represent tensions in millimetres of mercury; obviously they are much below the tensions of aqueous vapour in contact with water.

Percentage of H_2SO_4 in acid	Temperature								
	10°	20°	30°	40°	50°	60°	70°	80°	90°
44	4·4	8·5	15·5	28·1	48·3	—	—	—	—
48	3·7	7·1	13·4	23·9	40·1	69·0	107·2	—	—
52	3·0	5·8	10·9	18·9	31·5	54·0	84·5	131·2	207·9
56	2·2	4·3	8·1	14·2	24·1	41·6	65·0	100·9	160·0
60	1·6	3·0	6·1	10·0	16·9	28·7	46·1	72·3	118·7
64	1·2	2·2	4·0	6·5	10·9	18·7	30·3	48·0	83·7
68	0·9	1·5	3·0	4·5	7·2	12·3	19·4	31·4	56·0
72	0·7	1·0	2·0	3·2	4·8	7·5	12·0	20·0	33·7
76	0·4	0·5	1·4	2·1	3·0	4·8	7·5	11·8	18·5
80	0·2	0·3	0·8	1·3	1·9	2·9	4·1	6·2	9·3

Tension of nitrous anhydride dissolved in sulphuric acid at different temperatures. E. Sorel (*l.c. supra*) has made a number of determinations of the amounts of nitrous anhydride given off when sulphuric acid of different strengths, and containing different proportions of dissolved nitrous gases, was made to flow through a spiral tube 5 metres long placed in a water-bath at constant temperature, whilst a current of pure nitrogen gas passed through the spiral in the opposite direction; the results obtained varied from 0·009 milligram of N_2O_3 per litre of nitrogen at 0°, and 760 mm., when acid of sp.gr. 1·774, containing 28·4 grms. N_2O_3 per litre, was passed through at 40·1°, up to 109·15 milligrams, when acid of sp.gr. 1·597, containing 12·5 grms. N_2O_3 per litre, was passed through at 89·9°; in general, the weaker the acid and the higher the temperature the more N_2O_3 was evolved.

G. Lunge (Zeitsch. angew. Chem. 1891, 37; also J. Soc. Chem. Ind. 1891, 364) has carried out a large number of further observations on this point, employing substantially the same method, with the difference that carbon dioxide was used instead of nitrogen, and a 10-bulbed tube instead of a spiral. Pure nitrosulphonic acid dissolved in pure sulphuric acid was used; no nitric acid was found in the solution. The following tables, representing grms. per litre throughout, are abridged from those given for nitrous vitriol of gravity respectively 1·720, 1·686, 1·633, and 1·60, and for temperatures of 50°–90°. When plotted as curves, the figures show that in presence of strong acid, and at low temperatures, nitrosulphonic acid exists as a compound in the fluid; but, on diluting the liquid and raising the temperature, the compound is dissociated, and the nitrous acid formed removed by the gases into which it diffuses.

LOSS OF N_2O_3 AFTER 1 HOUR, DURING WHICH TIME 5 LITRES OF CO_2 WERE PASSED.

Originally present	50°	60°	70°	80°	90°
Nitrous vitriol, sp.gr. 1·72=78 *p.c.* H_2SO_4.					
1	—	—	—	—	0·006
5	—	—	—	—	0·037
10	—	—	—	0·018	0·093
15	—	—	0·006	0·056	0·193
20	—	—	0·031	0·150	0·356
25	0·012	0·031	0·125	0·312	0·600
30	0·081	0·125	0·293	0·550	0·956
35	0·156	0·312	0·525	0·868	1·375
40	0·268	0·500	0·775	1·193	1·800
45	0·406	0·712	1·050	1·537	2·337
50	0·550	0·931	1·325	1·875	2·675
Nitrous vitriol, sp.gr. 1·686=76 *p.c.* H_2SO_4.					
8	—	—	—	—	0·025
10	—	—	—	0·012	0·050
15	—	—	0·025	0·100	0·225
20	—	0·050	0·186	0·425	0·625
25	0·010	0·200	0·462	1·025	1·662
30	0·062	0·362	0·750	1·700	2·812
35	0·275	0·625	1·250	2·362	4·175
40	0·486	0·886	1·736	3·025	5·550
45	0·825	1·300	2·325	3·736	6·975
49	1·100	1·650	2·886	4·236	8·100
Nitrous vitriol, sp.gr. 1·633=71½ *p.c.* H_2SO_4.					
1	0·012	0·025	0·036	0·100	0·150
5	0·212	0·300	0·436	0·736	0·825
10	0·700	0·936	1·436	2·086	2·375
15	1·186	1·675	2·412	3·450	4·162
20	1·662	2·412	3·400	4·850	5·986
25	2·700	3·636	5·000	6·800	8·662
30	4·412	5·412	7·350	9·675	13·125
32	5·236	6·325	8·575	11·175	16·362

Loss of N_2O_3 after 1 Hour, during which Time 5 Litres of CO_2 were passed—*contd.*

Originally present	50°	60°	70°	80°	90°
Nitrous vitriol, sp.gr. 1·60=69 *p.c.* H_2SO_4					
1	0·050	0·086	0·175	0·336	0·412
5	0·812	1·150	1·500	2·120	2·700
10	1·975	2·812	3·712	4·990	6·475
15	3·360	4·612	6·125	8·400	10·625
20	4·700	6·425	8·562	11·850	14·800

Heat of solution of sulphuric acid. A considerable amount of heat is evolved on mixing sulphuric acid with water. Knietsch (Ber. 1901, 4103) gives the following table for the heats of solution of acids of different strengths.

SO_3 p.c.	H_2SO_4 p.c.	Calories	SO_3 p.c.	H_2SO_4 p.c.	Calories
50	61·25	39	67	82·08	93
51	62·48	41	68	83·30	98
52	63·70	44	69	84·53	103
53	64·93	46·5	70	85·75	108
54	66·15	49	71	86·98	113
55	67·38	51·5	72	88·20	119
56	68·60	54	73	89·43	126
57	69·83	57	74	90·65	133
58	71·05	59·5	75	91·88	139
59	72·28	62	76	93·10	146
60	73·50	65	77	94·33	152
61	74·73	68	78	95·55	160
62	75·95	72	79	96·78	168
63	77·18	75	80	98·00	178
64	78·40	79	81	99·23	188
65	79·63	83·5	81·63	100·00	193
66	80·85	88			

Fuming Sulphuric Acids.

Fuming acid is generally valued in proportion to the amount of trioxide present, the balance being H_2SO_4. The sp.gr. is sometimes employed as a test of strength, but is fallacious, since the density of acid containing about 60 p.c. of SO_3 is a maximum, both stronger and weaker acids exhibiting lower densities. The following table is given by R. Messel (J. Soc. Chem. Ind. 1885, 573), all the specimens being liquid at 26·6°.

Physical character at 60°F.	Percentage of SO_3	Specific gravity	
		At 80°F. =26·6°C.	Calculated to 60°F. =15·5°C.
—	8·3	1·842	1·852
Liquid . .	30·0	1·930	1·940
Crystalline mass resembling nitre	40·0	1·956	1·970
	44·5	1·961	1·975
	46·2	1·963	1·977
—	59·4	1·980	1·994
Liquid . .	60·8	1·992	2·006
	65·0	1·992	2·006
	69·4	2·002	2·016
Crystalline .	72·8	1·984	1·998
	80·0	1·959	1·973
	82·0	1·953	1·967

C. Winkler has obtained values slightly differing from Messel's, the acid used being 'commercial,' and therefore possibly not quite pure.

Specific gravity at 20°C.	Percentage of SO_3	Specific gravity at 20°C.	Percentage of SO_3
1·860	1·54	1·920	15·95
1·870	4·28	1·930	21·34
1·880	6·42	1·940	28·03
1·890	8·16	1·950	31·46
1·900	10·07	1·960	35·87
1·910	11·43	1·970	44·64

Knietsch (Ber. 1901, 4101) gives a more complete table of sp.grs. at 35°, also for commercial fuming acid, and in addition a series of observations at 15° and 45°. He finds that acid containing 60 p.c. free SO_3 has the maximum density at 15°, 56 p.c. free SO_3 at 35°, and 50 p.c. free SO_3 at 45°.

Specific Gravities of Fuming Acid at 35°C.

Free SO_3 p.c.	Sp.gr.	Free SO_3 p.c.	Sp.gr.	Free SO_3 p.c.	Sp.gr.
0	1·8186	34	1·9405	68	1·9600
2	1·8270	36	1·9474	70	1·9564
4	1·8360	38	1·9534	72	1·9502
6	1·8425	40	1·9584	74	1·9442
8	1·8498	42	1·9612	76	1·9379
10	1·8565	44	1·9643	78	1·9315
12	1·8627	46	1·9672	80	1·9251
14	1·8692	48	1·9702	82	1·9183
16	1·8756	50	1·9733	84	1·9115
18	1·8830	52	1·9749	86	1·9046
20	1·8919	54	1·9760	88	1·8980
22	1·9020	56	1·9772	90	1·8888
24	1·9092	58	1·9754	92	1·8800
26	1·9158	60	1·9738	94	1·8712
28	1·9220	62	1·9709	96	1·8605
30	1·9280	64	1·9672	98	1·8488
32	1·9338	66	1·9636	100	1·8370

A more accurate method consists in weighing out a portion of the acid to be examined in a sealed bulb, which is then broken under water by shaking up in a bottle; sulphurous acid, generally present, is first determined by titration with iodine solution, and then the SO_3 by precipitation as barium sulphate or volumetrically (Messel, *l.c.* p. 521). Lunge and Rey (Zeitsch. angew. Chem. 1891, 163) recommend a special form of bulb-tap pipette instead of a sealed bulb for this purpose. The table on p. 317 is abridged from a longer one given by Lunge and Hurter (Technical Chemists' Handbook, p. 134), for the reduction of percentages of total SO_3 thus found to percentages of SO_3, the balance being H_2SO_4.

Setlik finds (Chem. Zeit. 13, 1670; Chem. Soc. Abstr. 1890, 414; J. Soc. Chem. Ind. 1890, 417) that a simple method of valuation, with sufficient accuracy for most purposes, is to titrate 100 grms. in a flask with water until the acid ceases to give off fumes, the flask being kept cool. At first a thick cloud is formed on the addition of each drop, but latterly the fumes become less apparent. The flask must then be shaken after each addition of water until the fumes are

Total SO_3 found by analysis	Contains per cent.	
	SO_4H_2	SO_3
81·63	100	0
82·00	98	2
82·37	96	4
82·73	94	6
83·10	92	8
83·47	90	10
83·84	88	12
84·20	86	14
84·57	84	16
84·94	82	18
85·31	80	20
85·67	78	22
86·04	76	24
86·41	74	26
86·78	72	28
87·14	70	30
87·51	68	32
87·88	66	34
88·24	64	36
88·61	62	38
88·98	60	40
89·35	58	42
89·71	56	44
90·08	54	46
90·45	52	48
90·82	50	50
91·18	48	52
91·55	46	54
91·92	44	56
92·29	42	58
92·65	40	60
93·02	38	62
93·39	36	64
93·76	34	66
94·12	32	68
94·49	30	70
94·86	28	72
95·22	26	74
95·59	24	76
95·96	22	78
96·33	20	80
96·69	18	82
97·06	16	84
97·43	14	86
97·80	12	88
98·16	10	90
98·53	8	92
98·90	6	94
99·27	4	96
99·63	2	98
100·00	0	100

absorbed before adding the next portion: 1 c.c. of water represents 4·444 grms. SO_3. Acids containing more than 35 p.c. of SO_3 should be diluted down to about that strength by addition of pure H_2SO_4. Lunge regards this method as insufficiently accurate for use between buyer and seller, although otherwise convenient.

It may, however, be rendered quite reliable for practical purposes by using sulphuric acid of known strength instead of water.

Melting- and boiling-points of fuming acids. The following tables are given by Knietsch (Ber. 1901, 4100 and 4101).

Total SO_3 per cent.	Free SO_3 per cent.	Boiling-point.
82·3	3·64	212
83·4	9·63	170
86·45	26·23	125
89·5	42·84	92
93·24	63·20	60
99·5	97·2	43

Free SO_3 per cent.	Melting-point.	Free SO_3 per cent.	Melting-point.
0	+10·0	55	+18·4
5	+3·5	60	+0·7
10	−4·8	65	+0·8
15	−11·2	70	+9·0
20	−11·0	75	+17·2
25	−0·6	80	+22·0
30	+15·2	85	+33·0 (27)
35	+26·0	90	+34·0 (25)
40	+33·8	95	+36·0 (26)
45	+34·8	100	+40·0 (17·7)
50	+28·5		

The numbers in the brackets denote the fusing-points of fresh not yet polymerised acids.

Sulphur trioxide, or sulphuric anhydride, when quite pure and free from traces of water is a crystalline solid melting at 14·8° to a colourless liquid which boils at 46·2° (Weber, Ber. 19, 3187). The crystals are long transparent prisms similar to those of potassium nitrate. The presence of a trace of water renders this form unstable, and on standing for some time it changes to an asbestos like solid which begins to melt at about 50°, gradually passing back to the original form. Oddo (Chem. Zentr. 1901, 969) showed that the second modification was a polymer of the first, and should be represented by the formula S_2O_6. Schenck (Annalen, 316, 1) regards the more liquid modification as a solution of the asbestos like polymer in real SO_3 in a state of unstable equilibrium. Knietsch (Ber. 1901, 4100) gives the melting-point of pure SO_3 as 17·7°. On adding small quantities of water the melting-point is raised until at 85 p.c. free SO_3 it is 27° (maximum). On standing this polymerises; it no longer melts on heating, but

Specific Heats of Fuming Acids (Knietsch).

Total SO_3 p.c.	Free SO_3 p.c.	Sp. heat
76·4	—	0·3691
81·5	—	0·3478
83·46	10	0·3417
85·48	20·95	0·3391 (min.)
90·0	45·56	0·360
93	61·89	0·425
94·64	70·6	0·473
97	83·67	0·590
99	94·06	0·710
100	100·0	0·770

HEATS OF SOLUTION OF FUMING ACIDS (Knietsch).

SO_3 total per cent.	SO_3 free per cent.	Calories	Heat of solution of solid acids
82	2·0	199	
83	7·5	210	
84	12·9	223·5	
85	18·3	237·5	
86	23·5	250	
87	29·2	265	
88	34·7	278	
89	40·1	292	
90	45·6	308	286
91	51·0	325	304
92	56·4	344	322
93	61·9	363	340
94	67·3	381	360
95	72·8	401	380
96	78·3	421	402
97	83·7	442	423
98	89·1	465	442
99	84·6	490	463
100	100·0	515	486

sublimes and passes back again to the original modification.

Knietsch also gives tables of electric resistance, vapour tensions, viscosities, capillarity, and action on iron, and he has plotted them out graphically in a series of curves representing the properties of sulphuric acid both fuming and ordinary (Fig. 1) (J. Soc. Chem. Ind. 1902, 343).

These curves show that the acid containing 98·3 p.c. H_2SO_4, which is the maximum strength obtainable on concentrating weaker acids by heat, and which distils unchanged, has certain well-defined properties. It has the maximum boiling-point and minimum vapour tension. It has the highest specific gravity of any hydrated acid. Electrical resistance begins suddenly to rise at this point to a maximum at 100 p.c. H_2SO_4, and the action of the acid on iron decreases at the same time to a minimum.

Other features of these curves to be noted are—

I. Melting-point. Shows sharply defined maxima and minima at points representing definite molecular proportions of H_2SO_4 to H_2O or to SO_3.

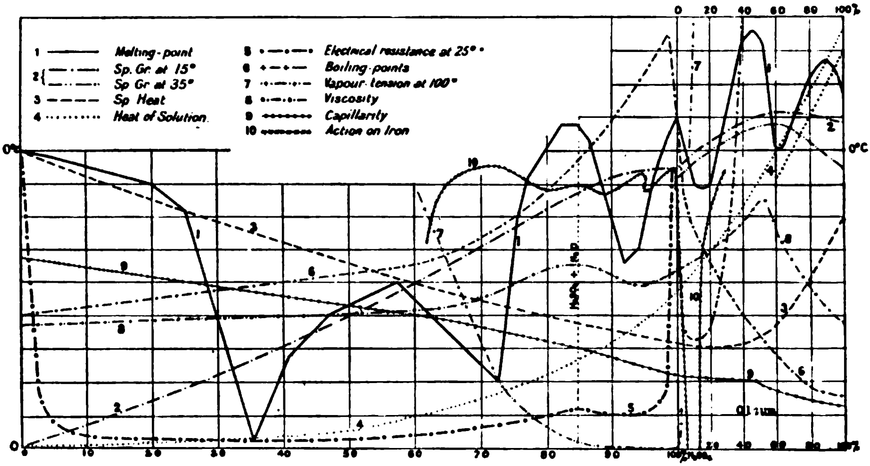

FIG. 1.

II. Density. Maxima at 98·3 p.c. H_2SO_4 and at 62 p.c. free SO_3.

III. Specific heat. Minimum at 20 p.c. free SO_3.

IV. Heat of solution. Rises steadily at increasing rate.

V. Electrical resistance. Great increase in conductivity caused by addition of a small quantity of acid to water. Indication of hydrate H_2SO_4,H_2O by small maximum there. Enormously rapid increase of resistance as H_2SO_4 approached (maximum resistance), and correspondingly rapid decrease on addition of SO_3 to H_2SO_4 until 10 p.c. free SO_3 reached, from which point there is again a rapid increase.

VI. Boiling-point. Maximum 98·3 p.c. H_2SO_4.

VII. Action on iron. Read from top of diagram. Maximum action at 10 p.c. free SO_3.

The action of sulphuric acids, both fuming and ordinary, on iron and lead is a matter of considerable importance, as these metals are used to a large extent in the processes of manufacture of these acids.

Cast iron. Acids of all strengths from chamber acid of 100°Tw. to 100 p.c. H_2SO_4 have very little action at ordinary temperatures, but if boiled in cast-iron vessels considerable action takes place with the weaker strengths, but it decreases as the acid becomes more concentrated, until at 98 p.c. H_2SO_4 the iron is scarcely attacked at all. Fuming acids below 20 p.c. free SO_3 have a somewhat greater action than 98–100 p.c. H_2SO_4, but above that strength the action practically ceases; but cast-iron vessels are not suitable for the manufacture of fuming acids, owing to the fact that the SO_3 penetrates into the pores of the metal causing strains (probably due to the formation of gases in the pores by action on the carbon) which cause them to suddenly crack without any warning.

On the other hand, wrought iron is unattacked by fuming acids above 27 p.c. free SO_3, but below that strength some action takes place, it being greatest about 10 p.c. free SO_3.

Wrought iron is acted on more rapidly than cast iron by acids below 100 p.c. H_2SO_4, especially at high temperatures, but in the cold the action is very slight with acids above 120°Tw., and wrought-iron or steel vessels are very largely used for conveying and storing acids of all strengths above 70 p.c. H_2SO_4.

Alloys of iron and silicon are much less attacked by boiling acids than iron itself, and vessels made of certain of these alloys (metillure and tantiron) may be used for concentrating even very weak acids up to 98 p.c. H_2SO_4. Fuming acids, however, energetically attack these alloys.

Lead. The action of acids up to 140°–150°Tw. is very slight even when heated to near the boiling-point of the acid, but if the latter is actually boiled the lead is strongly attacked. Above 150°Tw. up to 96 p.c. H_2SO_4 the action is still inconsiderable in the cold, but increases as the temperature rises, the lead being rapidly dissolved by ordinary concentrated sulphuric acid at about 250°–260°C. Monohydrate acts still more strongly, and fuming acids even at ordinary temperatures energetically attack this metal.

The impurities in ordinary lead have a considerable influence on its resistance to the action of sulphuric acid under different conditions. At ordinary temperatures, and even up to 100°C., the purest lead is least attacked by sulphuric acids concentrated or dilute. Impurities such as bismuth, antimony, zinc, or copper all have a harmful effect, but for very high temperatures approaching 200° as in the hottest concentrating pans the addition of a little copper (0·1–0·2 p.c.) appears to be of advantage (Lunge, Sulphuric Acid, vol. i. 209). The influence of physical condition and chemical composition on commercial lead for pan concentration of sulphuric acid has also been investigated by Hart (J. Soc. Chem. Ind. 1907, 504).

THE MANUFACTURE OF SULPHURIC ACID.

Two methods have been employed for the manufacture of sulphuric acid: (1) By decomposing natural or artificially prepared sulphates by heat, and (2) by burning sulphur or ores containing sulphur to sulphur dioxide, and further oxidising the latter to sulphur trioxide or sulphuric acid. Since about 1900 the first method has fallen into disuse, but before that time it had been employed for a great many years for making fuming acid, and it has been known for centuries, and was the original method by which sulphuric acid was first obtained.

During the last century, however, by far the larger quantity of acid has been obtained by the second method. If sulphur or materials containing sulphur are burnt in excess of air sulphur dioxide is produced, together with a little sulphur trioxide, and the oxidation of the sulphur dioxide is completed in one of two ways. 1. By the action of oxides or acids of nitrogen in the presence of steam or water; these oxides or acids act as carriers of oxygen from the excess of air present to the sulphur dioxide producing sulphuric acid more or less diluted with water. This is the basis of what is known as the chamber process, as it is carried out in large leaden chambers. 2. By the catalytic or surface action of certain substances, such as platinum, oxide of iron, &c., which under certain conditions have the power of causing the rapid combination of sulphur dioxide and oxygen to form sulphur trioxide. This is the basis of the contact process, and all fuming acid is now made by this method, and also a considerable amount of highly concentrated non-fuming or ordinary sulphuric acid.

THE LEAD CHAMBER PROCESS.

Early history. It has long been known that when brimstone and a small quantity of saltpetre are burnt together in moist air or in vessels containing water to absorb the fumes produced, an acid liquid results, which can be concentrated by evaporation. About 1740, Ward started a small factory at Richmond, Surrey, for the preparation of sulphuric acid by such a process. 8 parts of sulphur and 1 part of saltpetre were burnt together in a glass vessel shaped like a bell containing a little water at the bottom and kept warm on a sand-bath. As soon as the fumes from one charge were condensed, a second was introduced and fired, and this was continued until the acid was strong enough for use either at once or after concentration in glass retorts. The first improvement was the substitution by Roebuck in 1746 of lead vessels or chambers for glass bells; and 50 or 60 years later the use of steam from a separate boiler and of a continuous current of air with a sulphur burner separate from the leaden chamber were introduced. About 1818 a Mr. Hill of Deptford was the first to substitute pyrites for brimstone; in 1827 the Gay-Lussac tower for the recovery of the nitrous fumes carried away in the spent gas was invented, and in 1859 Glover built his first tower for denitrating the nitrous vitriol obtained from the Gay-Lussac tower, and for economising fuel by utilising the heat evolved in the combustion of the pyrites for concentrating the dilute chamber acid and supplying the chamber with a portion of the steam required for the process.

The essential characteristic of the chamber process is the action of the oxides of nitrogen in the presence of water in conveying oxygen to the sulphur dioxide, being reformed each time so that they react over and over again with successive quantities of sulphur dioxide, until the oxidation is practically complete; then the greater part of them may be recovered by absorption from the exit gas and introduced into the process again.

RAW MATERIALS FOR SULPHURIC ACID MANUFACTURE.

Brimstone. Commercial brimstone as used in the manufacture of sulphuric acid contains generally 95–98 p.c. sulphur, 2–5 p.c. ash, which is chiefly sand and calcium sulphate, and also a little bituminous matter. For European consumption the great bulk of it comes from Sicily.

A certain amount of sulphur recovered from alkali waste by the Chance-Claus process, and also from spent oxide of gas works, is used for acid making. The latter is usually dark-coloured owing to the presence of tarry matters. In the United States all the sulphur required for home consumption is obtained from Louisiana by the Frasch method of extraction (*v.* SULPHUR).

Technical analysis. Determination of moisture. 100 grms. are roughly crushed and dried at 212° in the steam oven until the weight is constant.

Determination of ash. 10 grms. are burnt in a tared porcelain dish and the residue weighed.

Direct estimation of sulphur (Macagno, Chem. News, 43, 192). 50 grms. of finely-ground brimstone are dissolved in 200 c.c. carbon disulphide in a well-stoppered bottle, and the specific gravity of the solution is determined at a given temperature *t*°. This is reduced to the sp.gr. at 15° by means of the formula

$$S = s \times 0{\cdot}00014\ (t-15)$$

(valid up to 25°), and the percentage of sulphur determined from the following table.

S	Percentage of sulphur	S	Percentage of sulphur
1·271	4×0	1·321	4×12·1
1·274	4×0·6	1·324	4×12·8
1·276	4×1·2	1·327	4×13·5
1·279	4×1·9	1·330	4×14·2
1·282	4×2·6	1·333	4×15·0
1·285	4×3·4	1·336	4×15·6
1·288	4×4·1	1·339	4×16·4
1·291	4×4·8	1·342	4×17·1
1·294	4×5·6	1·345	4×17·9
1·297	4×6·3	1·348	4×18·6
1·300	4×7·0	1·351	4×19·3
1·303	4×7·8	1·354	4×20·1
1·306	4×8·5	1·357	4×21·0
1·309	4×9·2	1·360	4×21·8
1·312	4×9·9	1·363	4×22·7
1·315	4×10·6	1·366	4×23·6
1·318	4×11·3	1·369	4×24·8

F. B. Carpenter (J. Soc. Chem. Ind. 1902, 832) states that if much gypsum is present, it interferes with the carbon disulphide treatment, and must previously be removed by boiling with hydrochloric acid.

Pyrites. Pure iron pyrites has the composition FeS_2, but commercial pyrites mostly contains more or less copper pyrites $Cu_2S{\cdot}Fe_2S_3$, together with varying amount of silicious gangue and small quantities or traces of arsenic, zinc, lead, antimony, selenium, mercury, thallium, &c. Its value is dependent quite as much on the quantity of copper present as on the amount of sulphur. The analyses given on p. 321 show the composition of the various kinds of pyrites that are, or have been, somewhat extensively used for the manufacture of sulphuric acid. It will be seen from the table that the sulphur may vary from 30 to about 50 p.c. The poorer ores, such as Wicklow containing only from 30 to 35 p.c. sulphur, are seldom used now, manufacturers preferring the richer Spanish and Norwegian ores, owing to the fact that the cost of handling and working pyrites is much the same, no matter what the percentage of sulphur may be, and at the same time the proportion of unburnt sulphur left in the 'cinders' will be the greater the lower the percentage in the ore before burning.

A certain quantity of pyrites is obtained in coal mining, and is picked from the coal (coal brasses). It always contains some adhering carbonaceous matter, which causes trouble in the chambers when it is burnt for sulphuric acid making.

Along the coast of the isle of Sheppey in Kent a considerable amount of pyrites has from time to time been collected on the beaches (having been washed out of the clay) and burnt for the production of sulphuric acid.

Analysis of pyrites. Determination of sulphur (Lunge's Technical Chemists' Handbook, 110). 0·5 grm. pyrites is heated with about 10 c.c. of a mixture of 3 volumes nitric acid (sp.gr. 1·4), and 1 of strong hydrochloric acid, solution being accelerated by heating now and then, and the whole is evaporated to dryness, heated with 5 c.c. more hydrochloric acid and evaporated again. The residue is moistened with 1 c.c. hydrochloric acid, and taken up with 100 c.c. hot water filtered and washed. The insoluble residue consisting of silica and silicates and perhaps some sulphates of lead or barium is usually ignited and weighed. The filtrate is heated with ammonia in slight excess, and after keeping hot, but not boiling, for 10–15 mins., the precipitated ferric hydroxide is filtered off and washed. If the filtrate and washings exceed 200 c.c. they are concentrated, slightly acidified with hydrochloric acid, heated to boiling, and 20 c.c. of a 10 p.c. solution of barium chloride (also hot) added. The precipitate is allowed to stand half an hour, the clear portion run off through a filter, and the residue heated with 100 c.c. of boiling water and allowed to settle 2 or 3 mins. This is again poured through the filter, and the washing by decantation repeated three or four times. The precipitate is finally transferred to the filter, washed, dried, and ignited, and the sulphur calculated from the weight of barium sulphate obtained. If the iron is not first removed a deficiency of 1–2 p.c. is apt to be occasioned owing to the solubility of barium sulphate in solutions of iron salts; whilst, on the other hand, a small quantity of ferric oxide is present in the ignited precipitate due to the precipitation of a double sulphate of iron and barium (Jannasch and Richards, J. pr. Chem. [ii.] 39, 321; J. Soc. Chem. Ind. 1889, 819). Lunge (Zeitsch. angew. Chem. 1889, 473; J. Soc. Chem. Ind. 1889, 966) finds that the precipitated ferric hydroxide may carry down some basic iron sulphate if the liquid is boiled until the smell of ammonia is all but gone, but not if the method is carried out as above described. A large number of other methods may be employed for the estimation of sulphur in pyrites, among which may be mentioned that of Fresenius (Zeitsch. anal. Chem. 1877, 335), in which the pyrites is fused with a mixture of sodium carbonate and potassium nitrate. That of List (Zeitsch. angew. Chem. 1903, 414), in which sodium peroxide is used, and Zulkowskys' method in which the pyrites is burnt in a stream of oxygen and the vapours are absorbed by potassium hypobromite solution.

To determine the sulphur left in the burnt ore, the material is dissolved in *aqua regia* and evaporated, the residue taken up with hydrochloric acid and water and precipitated as above by barium chloride whilst boiling, the removal of iron by ammonia being omitted.

J. Watson (J. Soc. Chem. Ind. 1888, 305) heats 3·2 grms. of the burnt ore with 2 grms. of sodium bicarbonate in a nickel crucible over

	Spanish and Portuguese			Norwegian		Irish (Wicklow)		Belgian	Cornish	Westphalian	French	
—	Tharsis		San Domingo	First quality	Second quality	Richer ore from Avoca	'Average'	—	Eight varieties	Meggen	Chessey and Sain-Bel (Lyons)	
	Highly cupriferous	'Average'	'Masons'									
Analyst	Pattinson	Alder Wright	Claudet	McCulloch	McCulloch	Pattinson	Alder Wright	McCulloch	Clapham	Pattinson	Mène	Scheurer-Kestner
Sulphur . . .	49·30	49·07	49·00	46·15	38·17	44·20	30·84	45·60	24·0 to 34·9	45·60	45·2 to 47·6	45 to 48
Iron	41·41	44·28	43·55	44·20	32·80	40·52	—	38·52	27·1 „ 60·7	38·52	39·0 „ 39·7	—
Copper . . .	5·81	2·75	3·20	1·20	1·10	0·90	1·29	nil	·4 „ 4·6	—	— —	1 to 2
Lead	0·66	—	0·93	—	—	1·50	—	—	0 „ 7·4	0·64	— —	—
Zinc	trace	—	0·35	2·10	2·32	3·51	—	6·00	0 „ 9·0	6·00	— —	—
Arsenic . . .	0·31	0·38	0·47	nil	trace	0·33	—	trace	0 „ 1·2	trace	present	—
Lime . . .	0·14	—	0·10	2·55*	11·90*	0·24	—	0·11*	0 „ 3·6*	0·11	— —	—
Silica and insoluble matter . . .	2·00		0·63	3·20	12·20	8·80	—	9·00	2 „ 38·7	8·70	9·6 to 11·0	—
Alumina, magnesia, oxygen, moisture, and matters not especially determined . .	0·37	3·52	1·77	0·60	1·51	0·34	—	0·77	—	0·73	3·9 „ 4·8	—
	100·00	100·00	100·00	100·00	100·00	100·34	—	100·00	—	100·30	— —	—

* Calcium carbonate.

low Bunsen flame for 5 or 10 mins.; the mass is then cautiously stirred with a wire stirrer, and the heat increased for 10–15 mins. more when the oxidation of the sulphur is complete. Finally, the mass is treated with water, and the excess of alkali titrated with standard acid, using methyl orange as indicator.

Lunge has investigated this method (Zeitsch. angew. Chem. 1889, 239; J. Soc. Chem. Ind. 1889, 572–1890, 1014), and finds that it is not only the simplest and cheapest, but also the quickest and most accurate test for the purpose.

Determination of arsenic. The method recommended in Lunge's Technical Chemists' Handbook is that of Reich, as modified by McCay. 0·5 grm. is decomposed by concentrated nitric acid, the solution evaporated nearly to dryness, and fused with 4 grms. Na_2CO_3 and 4 grms. KNO_3 for 10 mins. The mass is extracted with hot water, filtered, the filtrate acidified with nitric acid, and the arsenate precipitated with silver nitrate solution, the excess of acid being carefully neutralised with ammonia. The silver arsenate is dissolved in nitric acid, and the silver estimated by titration with ammonium thiocyanate, or the solution may be evaporated to dryness and the silver arsenate weighed.

Other metallic sulphides have recently come into considerable use for the manufacture of sulphuric acid, chiefly owing to legislation which has forced zinc and copper smelters to take measures to deal with the sulphurous gases liberated from their furnaces.

Zinc blende, which is the principal zinc ore, contains between 20 and 30 p.c. of sulphur, and the sulphur dioxide formed during the preliminary roasting process is very largely utilised for the production of sulphuric acid.

The following analyses of Rhenish blende are given by Minor (Chem. Zeit. 1889, 1602)—

Sulphur	30·24 p.c.	27·94 p.c.	22·11 p.c.	21·05 p.c.
Zinc .	27·76	31·92	40·29	37·81
Iron .	15·98	13·12	2·06	2·33
Gangue	21·02	27·02	35·54	38·84

The products from the roasting of copper ores and copper matte are now also largely used for vitriol manufacture.

The use of the **spent oxide** of gas-works for vitriol making has increased considerably during the last few years owing to its increased production. The sulphuretted hydrogen in coal gas is removed from it by means of a mixture of hydrated ferric oxide and sawdust, which can be made to take up so much sulphur by alternately exposing it to coal gas and air, that a product is obtained containing as much as 60 p.c. of sulphur available for conversion into sulphuric acid.

COMPOSITION OF SPENT OXIDE
(Davis, Chem. News, 36, 189).

	From precipitated $Fe(OH)_3$	From bog-iron ore
Ferric hydroxide .	17·74–19·36	15·96–26·42
Sawdust . . .	1·98–4·72	1·14–3·72
Calcium carbonate .	0–1·04	0–1·73
Ammonium thiocyanate	1·99–2·74	0·94–1·93
,, ferrocyanide	trace	trace–0·21
Tarry matters . .	0·72–1·22	0·92–1·14
Sulphur . . .	62·44–67·18	48·76–57·44
Insoluble in dilute HCl	3·66–5·47	9·74–11·42
Prussian blue . .		trace–0·17
Moisture (by difference)	4·72–5·76	7·22–10·82

Davis (Chem. News, 29, 30; 36, 189) gives a number of other analyses.

Sulphuretted hydrogen, recovered from alkali waste, and from ammonia liquor during the manufacture of sulphate of ammonia is sometimes used for the manufacture of sulphuric acid. It is burnt either by itself or in conjunction with spent oxide.

The available sulphur in spent oxide is usually estimated by extracting the free sulphur in a Sohxlet extraction apparatus by means of carbon disulphide and weighing it; but this method is not altogether satisfactory as the tarry matters are dissolved out also by the disulphide, whilst any sulphur existing in the insoluble form is not estimated. A more satisfactory method is to burn the spent oxide in a current of oxygen, and to absorb the evolved sulphur dioxide in bromine water, estimating the sulphuric acid formed by precipitation with barium chloride. Davis and Foucar (J. Soc. Chem. Ind. 1912, 100) convert the sulphur into sodium thiocyanate by digestion with alcoholic sodium cyanide solution, the thiocyanate being then titrated with N/20 silver nitrate solution in the usual way.

Nitrate of soda. In the early days of vitriol-making, *saltpetre*—*i.e.* potassium nitrate—was the only salt practically available; but this has so long been superseded by the cheaper 'Chile saltpetre' or 'soda nitre' (approximately pure sodium nitrate[1]) that the term *nitre* in the vitriol trade is always understood as referring to the latter.

PLANT USED FOR THE MANUFACTURE OF SULPHURIC ACID BY THE CHAMBER PROCESS.

In a modern sulphuric acid plant for the manufacture of chamber acid there are required: (1) A burner for the production of the mixture of sulphur dioxide, oxygen, and nitrogen; (2) an arrangement for introducing nitrogen oxides or nitric acid into the burner gas; (3) a steam generator; (4) one or more large leaden chambers in which the oxidation can take place; (5) a Gay-Lussac tower for recovering the bulk of the nitrogen oxides from the exit gases; and (6) a Glover tower for introducing these oxides again and concentrating the chamber acid.

The production of sulphur dioxide. Brimstone burners. The simplest form consists of a brick chamber covered by an arch, the bottom being formed by an iron plate. There is a door in front, through which the brimstone is charged from time to time, and at the back a pipe for taking away the gas. The burner is started by heating the iron plate by lighting a small fire on it, and when hot enough to ignite the sulphur, the latter is charged at regular intervals through the door, which slides in a frame and is adjusted by a chain and balance weight, the admission of the necessary amount of air being regulated by it. There is an air channel beneath the iron plate to prevent it from becoming too hot, and so

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[1] The average composition of sodium nitrate as used for vitriol making may be taken to be:

Sodium chloride . . .	0·5	
Sodium sulphate . . .	0·75	
Moisture	2·75	
Total 'refraction' (impurities) . . .		4·00
Sodium nitrate (by difference) . . .		96·00
		100·00

When the chloride present exceeds 1 p.c., the substance is apt to cause a considerable amount of loss of nitrogen oxides in the chambers.

causing the sulphur to sublime. The nitre pots containing the nitre and sulphuric acid may be placed in the midst of the burning sulphur, or better in a brick extension at the back of the burner. Several furnaces of this kind are usually combined together and charged at different times in order to obtain a gas of as uniform composition as possible. Each of them with plates 8 ft. by 4 ft. can burn 5 cwts. of brimstone in 24 hours. In some cases the gas passes from the burner into an upper chamber divided into two compartments, so that it has to pass from back to front and then back again before passing to a common flue; some additional air is admitted into this upper chamber in order to burn any sulphur which sublimes.

Harrison Blair's continuous burner consists of three parts. In front is a brick chamber into which the brimstone is charged either continuously by means of a hopper or at regular intervals. Here just sufficient air is admitted to keep up the heat of the furnace. The sulphur partly sublimes into a second compartment at the back, where sufficient air is admitted to complete the combustion, and the gas then passes to a chamber above in which the nitre pots are placed.

Fig. 2 represents Glover's brimstone burner. **A** is the burner plate fed by the hopper **B**; **C** is a chamber the upper part of which is filled with a network of firebricks, **D**, into which air is admitted by the pipes **F** to complete the combustion of the sulphur; **E** is a platinum dish, and **J**, **G** leaden pans for concentrating the acid; **K** flue to the Glover tower.

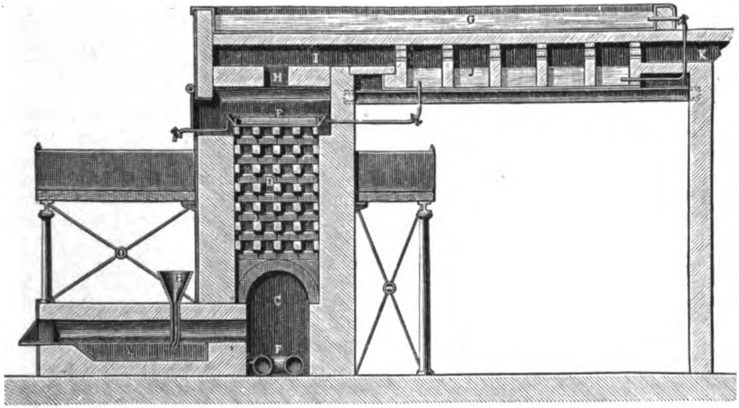

FIG. 2.

Pyrites burners. The bulk of the pyrites used for sulphuric acid manufacture arrives in large fragments which have to be broken either by hand or by crushing machines to a size suitable for burning. The broken ore is divided into 'smalls' and 'lumps' by screening through a ¼-in. or ½-in. sieve. The lumps should all pass through a screen with about 3-in. holes. Crushing machines produce more smalls than breaking by hand.

Burners for lump ore. These are generally known as kilns and they are constructed in such a way that the heat of combustion of the ore is utilised for maintaining the process without any extraneous fuel.

They are built in two rows back to back to avoid loss of heat (Fig. 3). The walls are of firebrick, the fronts being encased by cast-iron plates provided with various doors necessary for working. They are rectangular in section, and the ore in each kiln rests on a grate consisting of movable bars of 2-in. square section which can be rotated by a key which will fit on to the ends projecting through the front plate. By this means the space between the bars may be varied, being 2 ins. when their sides are vertical, and only 1¼ ins. when they are on edge. By rotating these bars the burnt ore is worked down into the ash pit below. The front of each kiln is also provided with a charging door about 2 ft. above the grate, and an ashpit door below the bars for removing the burnt ore. There is usually another opening between the charging door and the bars, which is only used occasionally when the ore forms slags or clinkers, which have to be raised and removed through the charging doors. The projecting ends of the bars are also boxed in and doors provided. The air admitted to each kiln is regulated by openings in the ash-pit doors. Fig. 3 shows a sectional elevation of two kilns built back to back. **A** is the charging door, **B** the small occasional working door, **C** the opening for turning the grate bars, and **D** the ash-pit door. The top of each burner is formed by a firebrick arch with an opening through which the gases pass to a common flue. These openings may be provided with dampers

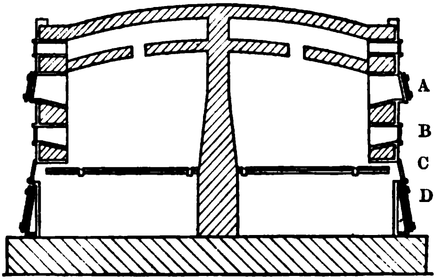

FIG. 3.

worked from the front. In some cases, usually in Continental works, the side walls do not completely separate the kilns, and the gases mix in the space above the burning ore, so that a common flue on the top of each row is not required. The ore may also be charged through the top by means of a hopper closed by a cone which can be lowered by a lever worked from the front of the kiln, and if the latter is well raised above the ground level the bottom of the ash pit may also be in the form of a hopper closed by a sliding door, so that the burnt ore can be dropped into a receptacle below the burner; or the ash pit may be made deep enough to allow the introduction of an iron bogie into which the burnt ore drops, and it can be thus expeditiously removed. The walls generally have a slight slope inwards below the charging door, so that the area at the grate bar level is a little smaller than that at the charging door. English burners are usually 4–5 ft. wide, and 4½–6 ft. from back to front at the grates. The depth of ore, which is determined by the height of the working door above the bars, may vary from 14 ins. to 2 ft. 6 ins., and depends usually on the percentage of sulphur in the pyrites, poor ores requiring a much greater depth than rich ores. In England for rich ores a depth of at least 2 ft. is employed, but on the Continent 16–18 ins. is more common.

In order to start a burner it is filled up with burnt ore up to about 3 ins. below the working door, and the top layer is brought to a dull-red heat by lighting a coke fire on the top. After about 24 hours the ore is hot enough, when the partially burnt coke is removed as far as possible, and the charge of pyrites is thrown in by the kiln-man and spread evenly over the surface. The amount charged will depend on the area of the kiln, the richness of the ore and the length of time between two successive charges. Usually with large kilns of 25–30 square ft. area the charge is put on every 24 hours, and with rich Spanish ore containing 48 p.c. sulphur, 6–9 cwt. is the weight charged, or from 30–40 lbs. per sq. ft. area. With poorer ores, such as Westphalian, containing 40–42 p.c. sulphur, 50–60 lbs. may be burnt per 24 hours per sq. ft. area (Hasenclever). Davis (Chem. Engineering, ii. 88) states that with Aguas Tenidas ore containing 50 p.c. sulphur he has burnt 55 lbs. per sq. ft. per 24 hours down to 1 p.c. sulphur, but the area employed only amounted to 14 sq. ft. With kilns of small area it is more usual to charge every 12 hours.

When the charge appears to be burnt off and shows no more sulphur flames (18–20 hours after charging for 24-hour charges) the surface is broken up by poking and raking, a certain amount of burnt ore being at the same time allowed to drop into the ash pit by turning the grate bars, and the burner gradually cools and is ready to charge again at the end of the 24 hours. The amount of air necessary is regulated by opening or closing the slides or holes in the ash-pit door as required. Usually 20–24 kilns are charged in rotation during the 24 hours, in order that the composition of the burner gas may be as uniform as possible. By the time the ore reaches the bars (5 or 6 days after it is charged) it should be nearly cold, and should not contain more than 3 p.c. sulphur, in the case of rich cupreous ores such as Rio Tinto or Tharsis pyrites. With non-cupreous pyrites the sulphur may be burnt as low as 1 p.c. The regulation of the draught requires considerable care. If too little is employed the ore will form slags or clinkers owing to the formation of fusible iron monosulphide FeS, and at the same time sulphur will sublime. These slags must not be allowed to get down on the bars, where they would stop the draught, but must be lifted by means of heavy pokers and broken up and pulled out of the working door. If the draught is too great the burners get cold and will not light readily when charged, and the burner gas will get too weak owing to the excess of air employed.

The air supply for a set of kilns is controlled behind the burners by means of a damper which may be placed either before or behind the chambers, and before each burner by holes in the ash-pit door. If the Glover tower and chambers are well raised above the kilns, or mechanical draught is employed, these means of control may be so regulated that no escape of gas takes place when the working doors are open for charging or poking, but at the same time a good deal of air enters and disturbs the uniform working of the chamber process; and this also happens when the ash-pit door is open during the removal of the burnt ore. Charging by means of a hopper in the top of the kiln, and discharging the burnt ore in a similar way below the ash pit, reduces this disturbance to a minimum. In many cases every time a working door is opened a good deal of gas escapes into the atmosphere; attempts have been made to prevent this by closing all the air slides in the ash-pit doors whenever a kiln is being charged (Norrington, Eng. Pat. 4131, 1878); or by connecting the ash pit when a door is open by means of a special flue with a chimney, the draught from which is so regulated that no burner gas is drawn down into it, but it is sufficient to prevent any blow out at the door during charging. The admission of air may also be checked from time to time by analyses made of the percentage of sulphur dioxide in the burner gas and of oxygen in the gases escaping from the chambers, the latter figure giving the average amount of surplus air admitted during the whole process of charging, burning, poking, &c.

Burners for smalls. At one time the use of smalls burners was mainly confined to the working up of the dust of the pyrites produced in transport or during breaking; if this does not amount to more than 7½ p.c. of the ore it may be burnt with the lumps if it be carefully distributed along the sides and back, and in the front corners of the kilns, leaving the central part free; or it may be made into balls or cakes after grinding up with water and drying on the top of the kilns; incipient oxidation takes place, and the mass binds together sufficiently hard to burn with the lumps. Formerly balls were made by the addition of clay and drying, but this method is no longer used, as the clay interfered with the burning and with the subsequent extraction of copper. During recent years large quantities of smalls have been received direct from the mines, being produced during the mining operations or from ore from which the copper has been extracted by weathering and washing out with water. Special smalls burners are necessary for burning these. In the earliest type, of which Spence's is an example, the ore was heated in a closed muffle or roaster by the flame from a coal fire, but this has long been superseded by arrangements requiring no extraneous heat. Sometimes the smalls are burnt on fire-clay shelves arranged above the burning pyrites in ordinary lump ore kilns, but this method has not proved satisfactory, much surplus air entering the burner during charging and removing the dust. Hasenclever and Helbig employed a series of alternate sloping shelves, one above the other in a square tower up which ordinary kiln gases passed, but this type of burner has become obsolete. In the Maletra furnace the heat of combustion of the smalls alone is sufficient to desulphurise the ore, and this type of burner has been worked successfully for many years both on the Continent and in England. As originally constructed, the burners are arranged back to back, there are six shelves to each, and each shelf is provided with a working door in front. In Schaeffner's modification (Fig. 4) the burners are arranged in a single row, there are seven shelves, the doors being alternately arranged four in front and three at the back. The chief drawbacks to this type of furnace are the considerable amount of labour required in working, and the excessive introduction of 'false' air during the frequent opening of the doors for the purpose of moving the ore from shelf to shelf. The cost of repairs for the furnaces is also considerable.

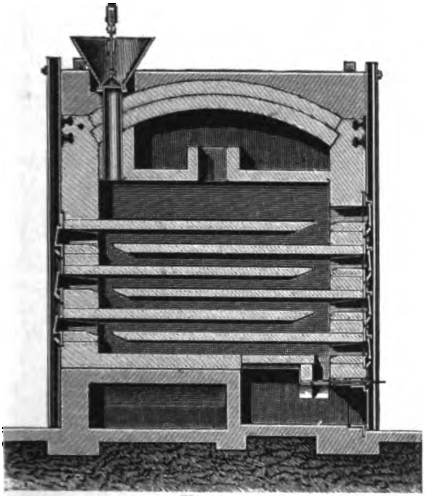

FIG. 4.

W. Crowder (J. Soc. Chem. Ind. 1891, 295) gives the following figures as the average of a number of daily tests of the sulphur contained in the partly-burnt ore on each of the seven beds of a Schaeffner kiln, charged with pyrites containing 50 p.c. sulphur every 8 hours, so that it took 56 hours for the ore to pass through the kiln from shelf to shelf.

No. 1 shelf . .	32·27	32·81
,, 2 ,, . .	21·41	17·55
,, 3 ,, . .	12·77	11·09
,, 4 ,, . .	6·39	5·03
,, 5 ,, . .	4·08	3·42
,, 6 ,, . .	2·35	2·56
,, 7 ,, . .	2·27	1·96

Mechanical smalls burners. The MacDougall furnace, patented in 1868, was the first burner of this type to be employed for burning smalls. It consists of a cast-iron cylinder, 6 ft. diameter by 12 ft. high, made in seven sections, bolted together, and is divided into seven chambers by fire-brick arches. Through the centre a vertical cast-iron shaft passes to which are attached a number of rakes, the teeth of which are so arranged that as the shaft revolves they move the ore alternately from centre to periphery and from periphery to centre on successive beds. The ore is continuously charged on to the top of the furnace by an elevator, and after travelling to the outer edge it drops into a receptacle from which it is continuously pushed into the top closed chamber by a ram, the rate of movement of which regulates the feed, and after passing from shelf to shelf is finally discharged at the bottom completely burnt. The air is continuously supplied by means of an air pump into the lowest chamber, and travels up the furnace in the opposite direction to the ore, the burner gas leaving the top section by a pipe leading to the chambers. The enormous amount of dust carried forward was the chief drawback to the MacDougall furnace when first introduced, and also the great wear and tear of the shaft and rakes due to excessive heat. The first-mentioned drawback was due to the small diameter of the burner, and the method of introduction of the air. The wear and tear was considerably reduced by making the shafts and rakes hollow and cooling them by air, and the dust carried away was somewhat reduced by substituting ordinary induced draught for the air pump, and providing dust chambers with perforated baffle plates for the interception of the dust (MacDougall, Eng. Pat. 3985, 1883). The MacDougall furnace has been further improved by Frasch, who employs water as the cooling medium for the shaft and rakes. Another modification is the Herreshoff burner (Fig. 5), in which the shaft is air-cooled. It is described by Gilchrist (J. Soc. Chem. Ind. 1899, 460). It consists of an upright steel shell lined with firebrick about 10 ft. high and 10 ft. diameter; the arms or rakes are inserted into sockets in the shaft and can be detached and replaced in a few minutes. There are five shelves with two rakes to each shelf. The ore is fed automatically from a hopper on to the top shelf by means of a plunger moving backwards and forwards, so much dropping at each revolution of the shaft. These furnaces will burn up to 3 tons of rich Spanish pyrites per 24 hours, between 2 and 3 p.c. of sulphur being left in the 'cinders,' and will furnish a richer gas than hand-worked furnaces. The hot air leaving the hollow shaft may be utilised for drying the ore by a suitable arrangement. The power required is about ⅔ h.p. per furnace.

Spence's mechanical furnace, patented in 1878, has met with some success in America (Lunge). It is a shelf burner of the Maletra type, provided with mechanical stirrers which travel to and fro from the front to the back of each shelf.

In the Kaufmann furnace, which is of the Herreshoff type, there are only three shelves, and the teeth on the rakes are so constructed that the ore is moved forward a certain distance, and then back a shorter distance during each revolution (Truchot, Proc. Seventh Int. Congr.

App. Chem. 1909; J. Soc. Chem. Ind. 1911, 280). The O'Brien furnace (U.S. Pat. 775147, 1904) is also a modification of the same type. The Wedge furnace represents the latest development of the mechanical burner. It can be constructed to burn 20 tons of pyrites per 24 hours, and is six or seven times as large as the ordinary Herreshoff burner. The shaft consists of a hollow steel cylinder, 4 ft. diameter, and its main feature is that it permits of repairs being made without interruption of its working (Hasenclever, J. Soc. Chem. Ind. 1911, 1291).

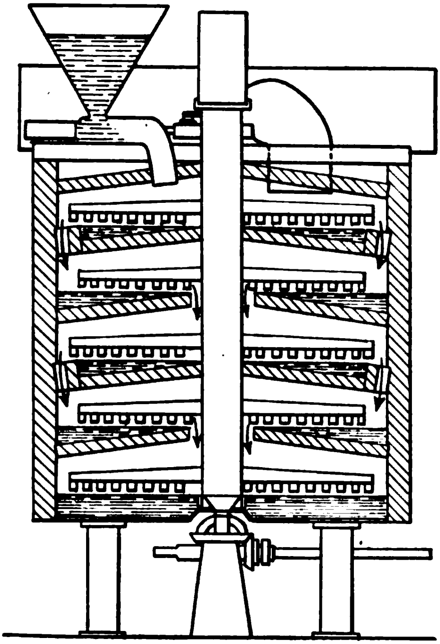

Fig. 5.

The new Herreshoff furnace (U.S. Pat. 976175, 1910) is also constructed to burn up to 20 tons pyrites per 24 hours. Both shaft and arms, which are hollow and of cast-iron, are cooled by forcing air through them by means of a fan. Part of the hot air so obtained is utilised for the combustion of the ore by introducing it into the lower beds, considerably increasing thereby the capacity of the furnace.

The chief advantage of the mechanical burner over hand-worked kilns is the saving of labour, but a good deal of this is counterbalanced by the cost of repairs. Lüty states (Zeitsch. angew. Chem. 1905, 1253) that hand-worked burners are cheaper than mechanical burners if the cost of labour is below 4*s*. per man per shift. An additional advantage is the regular composition of the burner gas obtained, owing to the fact that it is seldom necessary to open the doors of the furnaces.

Wherever smalls burners are employed it is necessary to provide a dust chamber to arrest the bulk of the dust carried forward from the furnaces. This chamber usually consists of a large expansion of the flue with or without baffle walls arranged in various ways, the main objects being to retard the speed of the gaseous current and to offer large surfaces on which the dust can deposit. At the same time the gas must not be too much cooled, nor must the baffle walls interfere seriously with the draught. If the surfaces are arranged in the direction of the current itself they do not seriously affect the draught, and yet collect a large amount of dust. With mechanical burners the amount of dust carried forward is very considerable, and it may contain as much as 10 p.c. unburnt sulphur. O'Brien's dust-catcher, described by Falding (Min. Ind. ix. 623) consists of a hopper-shaped iron shell 8 ft. wide at the top and 12 ft. high, lined with firebrick. The gas enters tangentially at the top and leaves by a central vertical pipe. The separation of the dust is due to centrifugal action, and it drops to the bottom and is discharged. 75 p.c. of the dust from five Herreshoff furnaces is retained by it. Benker and Hartmann (Fr. Pats. 372644, 1906; 387456, 1908) filter the gases and free them from dust by passing them horizontally through vertical filters composed of pieces of firebrick or burnt ore, the filtering material being continuously removed from the bottom and returned to the top after separating the dust.

Guttmann (J. Soc. Chem. Ind. 1903, 1331) states that good results have been obtained from tangential dust chambers on the principle of Meyer's acid chambers.

The Howard dust-chamber (U.S. Pat. 896111, 1910) consists of a brick chamber containing a large number of horizontal steel plates 2½ inches apart, between which the gases pass from one side to the other and deposit the dust on the large surface so obtained.

Furnaces for zinc blende. For this purpose, muffle furnaces were first employed, identical in principle with Spence's furnace for pyrites smalls, but not more than 60 p.c. of the sulphur could be utilised for sulphuric acid production from these, and they have been superseded by various forms of shelf-burner, which combine the heat produced by the burning of the ore with heat applied externally, but in such a manner that the fire gases are kept entirely separate from the roasting gases. Eichorn and Liebig (D. R. P. 21032) were the inventors of this type of furnace, by which the whole of the sulphur could be utilised for vitriol manufacture, and it has been modified and improved by Hasenclever in the Rhenania furnace, which consists of three superposed muffles, around which the fire gases circulate, and the ore is moved from one muffle to the next below, as in the Maletra furnace (Lunge, Sulphuric Acid, vol. i. 361; and Hasenclever, Chem. Ind. 1899, 25).

Of mechanical furnaces for roasting blende, Matthiessen and Hegeler's furnace has been worked successfully for a number of years in America at La Salle. It is a combination of Eichorn and Liebig's burner, with a stirring arrangement similar to Spence's. Hasenclever states that mechanical blende burners have not made much progress in Germany owing to the fact that the ores used contain lead and sinter when roasted, sticking to the moving parts and causing frequent stoppages (J. Soc. Chem. Ind. 1911, 1291).

Furnaces for galena. The gases from the roasting of galena or lead sulphide by the Huntington-Heberlein process are now used for sulphuric acid manufacture in several places in Germany; the working of these converters is intermittent, and a fairly continuous gas current can only be obtained by working a large number of converters charged at regular intervals. The Dwight-Lloyd furnace works continuously and can be made to deliver a regular gas current of 4–6 p.c. SO_2 by separating continuously the rich from the poorer gases and about 90 p.c. of the sulphur can be utilised for sulphuric acid manufacture (Hasenclever, *l.c.*).

Spent oxide of the gas works is usually burnt in a special kind of shelf burner (Hill's burner) of the Maletra type. MacDougall's furnace with four chambers only has also been used for a number of years for burning this material, and latterly a modification of the Herreshoff burner with three shelves has been introduced very successfully for this purpose.

The Harris mechanical furnace (Eng. Pats. 23331, 1910, and 25142, 1911) for roasting spent oxide (it is also used for pyrites) has special dust-trapped openings for discharging the oxide from bed to bed; it is said to require no dust-chamber (Chem. Trade J. Jan. 25th, 1913, p. 99).

Burners for sulphuretted hydrogen. Sulphuretted hydrogen, as obtained from ammonium sulphate works, may vary greatly in composition, and always contains a large amount of carbon dioxide; it is frequently burnt in conjunction with spent oxide in ordinary oxide burners or even in pyrites burners. As obtained from alkali waste in the Chance process, its composition is much more uniform, and it may be burnt by itself in a brick chamber provided with baffling walls which help to keep up the heat of the burner and also to mix the gases thoroughly and so ensure perfect combustion.

The burner gas. The quantity of air necessary for the complete combustion of sulphur in the different materials used for vitriol manufacture will vary considerably with the nature of those materials. Thus for free sulphur, pyrites, zinc blende, and sulphuretted hydrogen, the following equations represent the chief reactions taking place—

$$S+O_2=SO_2$$
$$4FeS_2+11O_2=8SO_2+2Fe_2O_3$$
$$2ZnS+3O_2=2SO_2+2ZnO$$
$$2H_2S+3O_2=2SO_2+2H_2O$$

which indicate that for a given weight of sulphur converted into sulphur dioxide the quantities of oxygen or air requisite will be in the proportion of 8, 11, 12, and 12 respectively. In addition to this, oxygen is required to convert the sulphur dioxide to sulphur trioxide, and a further excess is necessary to ensure the satisfactory working of the process. In the case of brimstone it is usual to employ such a surplus of air as will, after all the sulphur dioxide is oxidised and condensed, leave 5 p.c. oxygen in the exit gas, which corresponds to the following composition of the burner gas—

$$\begin{aligned} SO_2 &= 11{\cdot}23 \\ N &= 79{\cdot}00 \\ O &= 9{\cdot}77 \\ \hline & \quad 100{\cdot}00 \end{aligned}$$

For spent oxide no definite figures can be given, owing to the varying quantity of organic matter present.

For pyrites opinions differ as to the excess of oxygen required; Lunge considers 6·4 p.c. in the exit gas as about the proper amount, and the same for blende. Taking this figure the theoretical composition of the burner gases would be—

From pyrites	From zinc blende
$SO_2 = 8{\cdot}59$	$SO_2 = 8{\cdot}12$
$N = 81{\cdot}54$	$N = 82{\cdot}19$
$O = 9{\cdot}87$	$O = 9{\cdot}69$
100·00	100·00

(Lunge, Sulphuric Acid, vol. i. 398).

In addition to sulphur dioxide a certain amount of sulphur trioxide is always formed when these substances are burnt. In laboratory experiments with brimstone, Lunge found that 2·48–2·8 p.c. of the sulphur is obtained as sulphur trioxide, and 5·05 p.c. in the case of pyrites. In the latter case, the increased proportion is doubtless due to the catalytic action of the oxide of iron present, for if the gases be passed over a layer of hot ferric oxide, the percentage of sulphur trioxide may be largely increased. The author has found about 6 p.c. of the sulphur present as sulphur trioxide in the gases, both from lump burners and from smalls burnt in Herreshoff furnaces. From each lump ore burner the percentage may vary from 2 p.c., when the charge is freely burning and the sulphur dioxide is at its maximum, to 20 p.c. when the sulphur dioxide is a minimum and the charge is almost completely burnt. Lunge states that in blende roasting gases he has found as much as 25 p.c. of the sulphur present as sulphur trioxide. The presence of this sulphur trioxide affects the above-mentioned figures for the theoretical burner gas by reducing the percentages of sulphur dioxide and oxygen, and a further alteration is caused by the fact that the burnt ore contains some sulphates of iron and copper, which will also reduce the oxygen content slightly and increase the nitrogen, and also a little ferrous sulphide, the presence of which will have the reverse effect.

In practice brimstone burner gases generally contain from 10–11 p.c. sulphur dioxide, and the gases from rich pyrites 7–8 p.c. sulphur dioxide.

Analysis of the burner gas. Generally the process is controlled by determining the sulphur dioxide in the burner gas, and the oxygen in the exit gas. For the sulphur dioxide Reich's method is usually employed: a tube is inserted in the burner flue and the gas is aspirated slowly through a solution containing 10 c.c. N/10 iodine solution in 50 c.c. water, together with a little starch and sodium bicarbonate until the blue colour of the iodide of starch is discharged; the volume of water run out from the aspirating bottle+11 c.c. for the sulphur dioxide absorbed gives the volume of burner gas used from which the p.c. of sulphur dioxide may be calculated or taken from the following table (Lunge's Technical Chemists' Handbook, 117).

Volume of gas aspirated	P.c. SO_2 by volume	Volume of gas aspirated	P.c. SO_2 by volume
82	12	128	8
86	11·5	138	7·5
90	11	148	7
95	10·5	160	6·5
100	10	175	6
106	9·5	192	5·5
113	9	212	5
120	8·5		

Raschig (Zeitsch. angew. Chem. 1909, 1182) states that the addition of sodium acetate prevents nitrous acid from interfering with the iodine test for SO_2.

For the determination of oxygen the gas is first treated with caustic soda or potash to absorb any acid vapours or carbon dioxide present, and then the oxygen may be absorbed by phosphorus, alkaline solution of pyrogallol or ammoniacal cuprous chloride in an Orsat or similar apparatus. Alkaline pyrogallol absorbs oxygen very rapidly, only a few minutes being required for each test, but the solution does not keep well. With phosphorus about half an hour is required, and the temperature must be kept above 16°. Below that temperature the absorption is very slow. The phosphorus is employed in the form of thin sticks or beads, and is always kept under water except during its exposure to the gas which is being tested.

If the total acidity of the gas is to be determined a standard solution of caustic soda is employed with phenolphthalein as indicator. This will give the SO_2+SO_3 (Lunge, J. Soc. Chem. Ind. 1890, 1014). If the ore contain much organic matter, as when coal brasses or spent oxide are burnt, the carbon dioxide present will render this method inaccurate.

Comparison of brimstone and pyrites for sulphuric acid making. The advantages of using brimstone are—

1. Only about ⅔ of the chamber space is required as when pyrites is burnt owing to the burner gas being so much richer in SO_2; this means less cost of plant.

2. The burners give less trouble in working and require less labour.

3. The acid obtained is much purer than pyrites acid, being free from arsenic and iron.

But these advantages are mostly more than counterbalanced by the fact that in most countries pyrites-sulphur only costs about half the price of brimstone, and that for some of the largest applications of sulphuric acid (*e.g.* the manufacture by the Leblanc process of saltcake or crude sodium sulphate for glass-making and alkali-making, the preparation of superphosphate, ammonium sulphate, and artificial manures generally) the impurities in pyrites acid are of little or no importance.

For manufacturing articles of food, for storage batteries and certain other purposes, these impurities are harmful, and there is still a certain amount of brimstone acid made in this country for these purposes, but it is gradually being displaced by purified pyrites acid from which the arsenic has been eliminated by precipitation as sulphide and filtration, and by acid made by the contact process in which the burner gases have to be purified to such an extent that an acid is obtained quite equal to brimstone acid in purity. Acid made from spent oxide of gas works, being practically free from arsenic, is also used in many cases in place of brimstone acid.

In America (where the disproportion between the price of brimstone and pyrites suitable for vitriol-making is, in many localities, not so great as elsewhere) the manufacture of brimstone acid is still carried out to a considerable extent, but even there during the last few years the use of pyrites and other sulphur ores has enormously increased.

Apparatus for introducing nitrogen oxides. There are two chief ways in which the nitrogen oxides are introduced into the burner gas. In the first, nitric acid is evolved from a mixture of sodium nitrate and sulphuric acid introduced at intervals into an iron pot placed in the hot burner gas flue; whilst in the second, nitric acid is introduced in the liquid form either in the Glover tower along with the nitrous vitriol or into the first chamber.

Opinions differ as to the relative advantages of the two methods, the potting system being mostly in favour in Great Britain, whilst Continental manufacturers more often employ the liquid acid method. The points in favour of the latter are the following: A more uniform introduction of the nitric acid vapours is possible than in the potting system, the admission of 'false' air, which takes place when the pots are charged or discharged, is avoided, and if at any time an extra supply of nitrogen oxides is temporarily required it can be instantly procured by increasing the rate of flow of the nitric acid. On the other hand, the use of liquid acid involves extra cost in distilling the acid, and more outlay for labour, carboys, and appliances for introducing it into the process, and when introduced into the chamber it may cause corrosion of the lead if not completely vaporised before reaching the bottom; this danger, however, is completely avoided by introducing it into the Glover tower.

The nitre pot system as first applied to brimstone burners was carried into effect by placing the cast-iron pots containing the mixture of nitre and sulphuric acid on the floor of the burner. As, however, they frequently frothed over and damaged the burner, they are now always placed in an extension of the latter where they are heated by the hot burner gases.

With pyrites burners the pots are usually placed in a separate nitre oven, practically an enlargement of the flue just beyond the last kiln with a door in front for introducing them and withdrawing them by means of a stout fork. The bottom is protected by a cast-iron tray to catch boilings-over, and the pots are charged at regular intervals in order to keep as equable a supply of nitrous vapours as possible. Every time the oven door is opened much air gets into the flues, and much gas escapes, and to avoid this the following arrangement is now frequently employed. There are usually two pots, each large enough to hold ½ cwt. of nitre; they are fixed in the flue, and each is provided with a tubular spout at one end, which is plugged up when in use, and projects outwards from the oven. From 7 to 14 lbs. of nitre are charged into the pots alternately at regular intervals through a small hopper in the top of the oven, and a slow stream of sulphuric acid is run on to it by means of an S-shaped tube from a small tank provided with a stop-cock to regulate the rate of flow, so that a steady stream of nitric acid is liberated during each interval of charging; when about 56 lbs. of nitre have been worked off, the outlet plug is removed, and the fused nitre cake (acid sodium sulphate often designated Sally Nixon, *i.e.* sal enixon) is allowed to run out into a cast-iron saucer where it solidifies.

When the liquid acid method is employed, if there is no Glover tower the acid is introduced into the first chamber (usually a small preliminary one), being made to run intermittently or regularly over some distributing arrangement, exposing a large surface; such as a tall pyramid of glass or stoneware dishes or cylinders of such dimensions that the whole of the acid is volatilised before it reaches the lowest dish, which, however, should be provided with an overflow pipe to take away any acid which escapes vaporisation out of the chamber in order to prevent serious corrosion of the lead.

The acid may be introduced at a uniform rate by means of a Mariotte's bottle in which a constant pressure of liquid is maintained by only allowing the air to enter by a tube reaching down to within a short distance of the outlet.

Another method is to spray the acid into the chamber by a steam jet analogous to the arrangement used by Sprengel for spraying water. The best and simplest method is, however, to feed the acid in along with the nitrous vitriol and chamber acid at the top of the Glover tower; for although at one time it was thought that this mode of supply was likely to cause loss of nitre, experience has shown that there is no increase in the consumption when this method was substituted for the cascade system (Lunge).

Where the sulphuric acid is intended for the manufacture of saltcake or superphosphate the nitric acid is sometimes introduced as a solution of nitre in water or dilute sulphuric acid, either by spraying into the chambers or running through the Glover tower. In the chamber there is the danger that it may reach the bottom acid undecomposed and cause corrosion, whilst stoppage from crystallisation of solid sodium sulphate is apt to occur when it is used in the Glover tower.

Occasionally the chambers are fed with nitrous gases obtained as by-products. Lunge states that at the Uetikon works near Zurich nearly all the nitre required for the chambers is obtained in the manufacture of ferric sulphate (iron mordant) by treating ferrous sulphate with nitric acid.

The lead chambers. These are usually placed at a considerable height above the ground, and are supported on brick or stone walls or piers, or on pillars of wood, or cast-iron columns. The space below can be used for storage purposes, or even for the pyrites kilns if high enough. On these piers or walls are placed stout wooden beams which carry the transverse joists which support the chamber bottom. These joists project several feet beyond the chamber frame in order to allow for passages between and around the chambers, and they are covered with a smooth wooden floor. In some cases the beams are arranged from pier to pier across the width of the chamber and the joists then run in a longitudinal direction. Upon this floor the chamber frame is erected. The sides consist of two stout horizontal rectangles of wood, the sole-tree or sill, and the crown-tree or capping, connected by uprights or standards, which are mortised into them, and further tied by cross rails or stays. The crown-tree carries the transverse joists to which the roof of the chamber is attached. American pitch pine is usually employed for this framework, and is the best timber for the purpose, and wherever acids are concerned.

The chamber itself is usually constructed of sheet lead of such a thickness as to weigh 6 lbs. per square foot, occasionally 7 lbs., especially for the first chamber of the series, which being the hottest is the most readily attacked. In America 5 lb., or even 4 lb. lead is sometimes employed. The sides and roof are attached to the wooden framework by means of lead straps which are nailed to the uprights or cross rails and to the roof joists, the nails having lead-coated heads to enable them better to resist corrosion. These straps are burnt to the sheet lead by the flame of a blowpipe burning hydrogen in compressed air, or coal gas may be used with compressed oxygen from a steel cylinder. Usually the sheets themselves are similarly fused together, but sometimes unfused rabbet joints are employed, made by folding the edges over and then beating down flat. The roof and sides are burnt together at the crown-tree, and sometimes the bottom is also fused to the sides so that the whole chamber forms one gigantic water- and gas-tight leaden box; but more frequently the sides are suspended like a curtain in a large flat dish made by turning up the edges of the bottom 12 or 15 ins. or even to a greater height up to 2 ft. 6 ins. if much acid storage room is required, and the construction will allow it. This dish or saucer is always kept luted with acid when the chamber is at work, and the upstand is protected all round by a 1-in. board to resist the outward pressure of the acid.

In Great Britain the chambers are seldom roofed in, the tops sloping slightly from one side to the other to allow the rain water to run off into a gutter, but the sides are usually protected from the wind by light wooden or corrugated iron walls. On the Continent, however, where the variations in temperature from summer to winter are greater, they are usually completely enclosed in buildings. Wherever possible the lead should be kept clear of the wooden framework of the chamber in order to allow efficient air cooling, the lead being more rapidly attacked where it is in contact with the wooden uprights, joists, &c. At some places the chamber frame is made of angle iron. In the Moritz system of construction (Fr. Pat. 395694, 1908; Chem. Trade J. 1911, 493) a strongly built skeleton of iron encloses the chambers, which are suspended from overhead beams by tie rods attached to the walls by lead strips; the top of each chamber is arched to prevent the accumulation of dust and to avoid dead corners, and the floor rests on perforated sheet iron supported by brick columns; the upturned edge is also iron plate bent under the floor. The advantage claimed for this system is the uniform cooling which takes place, and which prevents local corrosion such as ensues where a wooden frame is in contact with the lead.

Chambers are usually of rectangular shape, 100–130 ft. long, 20–30 ft. wide, and 16–25 ft. high. They have been constructed up to 300 ft. in length, where there is only one large chamber employed. Since the introduction of water spraying instead of steam the tendency has been to increase the height to 25–33 ft., and at the same time to make them narrower, not more than 20 ft. wide. At the Rhenania Chemical Works the top corners are cut off to suit the shape of the roof and avoid dead corners (Lunge). The annular chambers of

Delplace (Eng. Pat. 5058, 1890) have been tried in several places, but do not seem to offer any advantages over those of the ordinary rectangular shape. Meyer's tangential chambers of circular or polygonal section (Eng. Pat. 18378, 1888) have been erected at a number of works on the Continent; the gas enters tangentially on the upper part of the sides, and the outlet pipes are in the centre of the bottom (Chem. Zeit. 1899, 296; Zeitsch. angew. Chem. 1899, 656; 1900, 739; 1901, 1245).

In England all the chambers are generally of equal size, three or four forming a set and taking the gas from one set of kilns; or five or six chambers may be combined and take the gases from two sets of burners, the fifth and sixth being common to the two sets; but in France one large chamber is frequently employed with small ones before and behind it. Hasenclever (Chem. Ind. 1899, 26), at the Rhenania Works, combines two large chambers with two small back ones, whilst other manufacturers prefer three chambers in series decreasing in size from the first to the last.

The capacity of each chamber varies between 25,000 and 70,000 cb. ft., but occasionally they may be constructed as low as 10,000 cb. ft., or as high as 140,000 cb. ft. The total capacity of a set is seldom more than 200,000 cb. ft., but Hasenclever mentions the existence of sets of 420,000 cb. ft. capacity. The average capacity will probably be between 100,000 and 150,000 cb. ft. Meyer's tangential chambers are usually about 33 ft. in diameter and 26 ft. high, and are combined in sets of three (66,250 cb. ft. total capacity). Falding (Eng. and Mining J. 1909, 441; U.S. Pat. 932771, 1909) recommends the use of one large chamber of such a height that its vertical axis is in the proportion of 3 to 2 over any horizontal axis. Small chambers require more lead and occupy more space than large ones of equal capacity, and it is taken as a practical rule that for every cubic foot of chamber space there should be about 0·2 sq. ft. of total surface (top, bottom, sides, and ends).

The different chambers of a set are sometimes arranged so that each is a few inches higher than the preceding one in order to enable the weaker acid produced in the last chamber to be run back into the stronger first chamber, and to get rid of traces of nitre which it usually contains. If the chambers are on the same level injectors are used for this purpose.

The connections between the chambers may be circular or rectangular in section, and are usually constructed of 10–12 lb. lead, those of the latter shape being supported by a wooden frame-work, whilst the round pipes are held in position by means of iron hoops with wood laggings. Considerable difference of opinion exists as to where they should leave and enter the chambers, some being of opinion that the gases should leave each chamber near the top and enter the next near the bottom, while others prefer the reverse arrangement. According to Lunge and Naef's experiments, it is a matter of indifference where the connecting tubes are placed, but Porter (J. Soc. Chem. Ind. 1902, 476), after describing some experiments with a glass model to show the path which gases travel in the chamber, recommends that they should enter near the bottom and leave near the top of each chamber.

There is a certain definite relationship between the total cubic capacity of a set of chambers and the quantity of acid produced in a specified time. The number of cubic feet of chamber space required for condensing the acid from 1 lb. of sulphur burnt in 24 hours (the form in which it is usually expressed in England [1]) will depend on a number of different factors. It will be less for brimstone than for pyrites, owing to the difference in the composition of the burner gas; it will be less for rich pyrites than for poor for a similar reason; other things being equal it will depend on the proportion of nitre used, a larger consumption compensating for a smaller chamber space; it will also depend on the presence or absence of Glover and Gay-Lussac towers, and likewise on the size and efficiency of those towers. It will be less in winter than in summer, owing to the lower temperature and increased density of the gases in the colder season, and it can be reduced by a number of different arrangements for cooling the gases and the chambers, which will be referred to later.

Generally speaking, where Glover and Gay-Lussac towers are not used, 25–30 cb. ft. of chamber space per lb. of sulphur burnt per 24 hours will be required. If moderate-sized towers are used 16–20 cb. ft. will be sufficient, and by increasing the size of these towers it may be reduced to 10–11 cb. ft., as in the intensive system, but in the latter case the wear and tear of the chambers will be very considerable, unless steps are taken to keep the temperature in them from rising too high. The working of the process also requires more supervision. These figures are for pyrites; for brimstone the chamber space need only be about 75 p.c. of the above figures.

Opinions differ among manufacturers as to how long it is possible to work a chamber economically. Generally speaking after 10 years' work the repairs required to keep a chamber in good working order are very considerable, and many are of opinion that it should then be rebuilt, losses through leakages, injury to the frame work, and cost of patching will more than counterbalance the cost of re-erection. On the other hand, where chambers are well constructed and the process is well controlled and not forced, they have been known to last 20 or even 30 years, with occasional stoppages for repairs after the first 8 or 10 years.

Burgemeister (Chem. Zeit. 13, 1633; also J. Soc. Chem. Ind. 1890, 66) has made various measurements of the rate of diminution in thickness of the lead in a set of two chambers, one of which had lost 26·8 p.c. after working 210 months, and the other 17·65 p.c. of its thickness after 120 working months. The latter was a small chamber placed between the Glover and the large chamber first mentioned, and kept at a higher temperature.

Arrangements for supplying steam or water to the chambers. When no Gay-Lussac and Glover towers are used all the water ultimately transformed into chamber acid must be supplied in the form of steam or water spray. If the strength of the chamber acid is 120°Tw.=68·7 p.c. H_2SO_4, 1·96 parts water will be required for

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[1] On the Continent the number of kilogrammes of H_2SO_4 produced per cubic metre per 24 hours is the form in which the chamber space is expressed.

each part of sulphur burnt; if towers are employed, and the average strength of the acid obtained is 145°Tw.=79·25 p.c. H_2SO_4, the water required will be equal to 1·44 times the sulphur burnt.

This is usually introduced into the chambers in the form of steam generated in an ordinary steam boiler. At one time this was sometimes mounted on the burners so as to utilise the heat of combustion of the pyrites, but this arrangement has been given up everywhere since the introduction of the Glover tower. The pressure required need not be more than sufficient to carry the jets of steam well into the chamber, say 5–10 lbs. per square inch, but is very important for the regular working of the process that it should be kept uniform; to ensure this, automatic regulators are employed in some works to keep a uniform pressure in the steam main, no matter what the boiler pressure may be. The exhaust steam of engines may be utilised for supplying the chambers, provided that they are worked in such a way as to leave a definite pressure in the exhaust. Fig. 6 represents a steam jet, the tube CC passing into the chamber through the wall EE by a stuffing box DD, B being the regulating cock, A the connection with the steam main, and FG a mercurial gauge affixed by means of T-joint H so as to indicate the pressure of the entering steam.

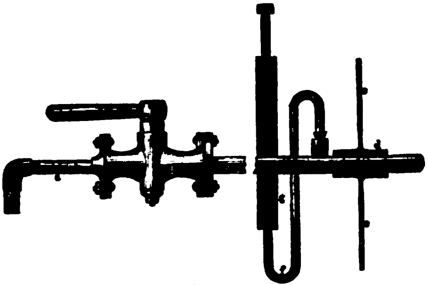


FIG. 6.

Practice differs considerably in different countries, and amongst different manufacturers, as to the method adopted for introducing the steam so as to mix uniformly with the burner gases. In England frequently only one jet is employed for each chamber, placed somewhere near the inlet pipe or a little above the centre of the chamber end, but on the Continent the practice is to employ a number of jets at right angles to the direction of the gaseous current either in the long chamber sides near the top, or through the roof of the chamber. The regulation is certainly much simpler and easier in the former method, but the distribution of the steam cannot be so well controlled as in the latter. Where a Glover tower is used the first part of the first chamber requires little or no additional steam to that entering with the gases, and therefore the first steam jet should be some distance from the front end of the chamber. Jets introduced at the far end in opposition to the direction of the gaseous current are sometimes employed, but tend to impede the draught.

In 1873 Sprengel patented the employment of pulverised water, *i.e.* water reduced to a mist-like spray by blowing a jet of steam at about 2 atmospheres pressure through a platinum nozzle in the centre of a water jet; with a properly proportioned compound jet, 4 parts by weight of water can be converted into fine spray by 1 of steam. The spray does not carry as far as a steam jet, wherefore in a large chamber a number of jets are necessary, and are placed in the sides about 40 ft. apart, and supplied with water from a tank fixed at some height above. The advantages claimed for the use of spray instead of steam are, that not only is fuel saved, but the temperature of the chamber is lowered so that more acid can be produced in a given chamber space. Sprengel's apparatus was worked for a number of years at Barking, but was given up on the introduction of Glover and Gay-Lussac towers there, and has practically gone out of use.

On the other hand, pulverised or atomised water (produced by the mechanical action of a fine stream issuing under a pressure of 2 atmospheres from a platinum nozzle on to a platinum button) has been successfully applied for a considerable number of years at Griesheim (Lunge), and has lately come into more general use where the intensive system of sulphuric manufacture is worked. Two rows of water jets, 20 ft. apart, are introduced through tubes in the chamber tops, and the water has to be specially filtered to avoid blocking up the fine jets used. For narrow chambers only one row of jets is employed. Where the intensive system is worked the use of atomised water has been of great service in keeping down the temperature of the chambers, and so preventing rapid wear and tear and excessive nitre consumption. Kestner (J. Soc. Chem. Ind. 1903, 334) gives the following calculations showing the effect of replacing steam by water sprays—

Heat of formation of $H_2SO_4+3H_2O$ (approx. chamber acid) . . =65,500 Cal.
Heat given up by condensation of steam at 120° to 60° . . =41,976 „
Total heat . . =107,476 „

If the steam is replaced by water at 15°—

Heat of formation of $H_2SO_4+3H_2O$=65,500 Cal.
Heat absorbed by water raised from 15° to 60° . . . . =3,240 „
Total heat . . =62,260 „

The difference in the two cases is thus, 45,216 calories.

If the average strength of the acid produced is represented by $H_2SO_4,2H_2O$, which will more nearly represent the correct strength when the Glover tower acid is taken into consideration, the difference in the heat of the reaction will be=33,910 calories. Water sprays cannot entirely replace steam, which is usually required in the last chamber, and also in the other chambers in very cold weather in order to prevent the temperature falling below a certain minimum, which Benker considers should be 60–65° for the first chamber (Kestner, J. Soc. Chem. Ind. 1903, 334). For this reason water spraying is of very little use in non-intensive working, except in very hot weather.

A special platinum jet for converting water or acid liquids into spray has been constructed by Benker in which the distance between the nozzle and the disc is adjustable, the disc being moved backwards and forwards by a rod at the end of which is cut a fine thread which works in a similar nut above. The jet is easily cleaned.

Korting Bros. have introduced a spray producer which gives the liquid a rotating movement, so that, issuing from the jet, it is projected in a conical spray. The nozzle is of platinum usually, but it can be replaced by a glass jet fitted into a hard lead nozzle by a small indiarubber washer. These spray producers have proved very successful, and have been used for a number of years in Continental factories (Lunge).

Guttmann (Eng. Pat. 18927, 1906) has patented the spraying of acid from the back chambers into the first and second chambers instead of steam or water; stronger chamber acid is obtained, and no harm is done if the spraying apparatus is defective.

Raschig (J. Soc. Chem. Ind. 1911, 172) has also suggested the spraying of weak sulphuric acid into the chambers instead of water, so as to avoid the possible reduction of the higher oxides of nitrogen to nitrogen monoxide or nitrogen.

The quantity of steam or water spray introduced into the chamber is regulated so as to produce an acid of a definite strength; and drips or tell-tales consisting of earthenware or leaden trays are placed inside the chambers to catch a certain amount of the condensing acid which runs through a tube into a lead or glass cylinder outside the chamber, and can there be tested from time to time; or samples can be obtained of the acid condensing in the connections between the chambers and tested at intervals in the same way.

In order to draw off acid from a chamber, a small leaden box is placed on the floor close by, open at the top, and of the same height as the upstand of the chamber bottom, and is connected at or near the bottom with the chamber by means of a pipe. In the bottom of this box is a seating of regulus metal (a hard alloy of lead and antimony) closed by a plug; on lifting this plug the acid in the box runs away through a pipe attached to the seating, and at the same time more acid levels into the box from the chamber. By allowing the acid to enter the box through a seating which can be closed by a plug, the same box may be used for two or more chambers. Another method is to siphon the acid from the chamber into the box by a siphon with a cup attached at each end in order to keep it always full when not in use, so that it starts to act as soon as one limb is put into the acid.

Arrangements for production of draught. The draught necessary for moving the acid gases through a set of chambers may be produced in several ways. In the first place, the hot burner gases are lighter, bulk for bulk, than air at the ordinary temperature, and consequently tend to rise and produce an indraught at the burners and a pressure in the chambers. The hotter the gases, and the higher they have to rise before they enter the Glover tower or chambers, the greater will be the draught due to this cause. At the end of the system the outlet pipe is usually connected with a chimney which assists in drawing the gases through the chambers, or else the outlet consists of a vertical pipe from the last chamber or tower; this has a slight aspirating action, owing to the exit gases being lighter than the air, which may be increased by means of a simple jet of steam, or better, by a Korting's injector. The formation of sulphuric acid itself in the chambers also acts as a cause of draught, the volume of the gases being reduced by the amount of condensation taking place.

For the regulation of the draught dampers are usually provided between the burners and the chambers, and in the outlet pipe at the end of the system.

Where a chimney is employed, any great variations in the draught from this may be corrected by a damper or throttle valve, which is automatically worked from a lever, on the other end of which hangs a bell standing in an annular lute containing water or other suitable liquid. The air in the bell is connected with the exit pipe beyond the damper, so that, when the draught from the chimney increases the bell descends in the lute, thus causing the other end of the lever to rise, partially closing the damper; the reverse happens when the draught decreases. Latterly the employment of fans for producing the necessary draught by mechanical means has very largely increased. These are usually made of iron covered with lead, of antimonial lead or of stoneware, and are generally placed between the last chamber and the Gay-Lussac tower, or if there are two of the latter towers, between them (Kestner, J. Soc. Chem. Ind. 1903, 334; Benker, Zeitsch. angew. Chem. 1903, 861). They have also been placed between the Glover tower and the first chamber, but lead or antimonial lead is rapidly corroded there (Niedenführ and Lüty, *ibid.* 1902). Falding employs two fans, one behind the Glover tower to regulate the draught of the burners, and the other in front of the Gay-Lussac (Min. Ind. vii. 672).

Mühlhaüser (Zeitsch. angew. Chem. 1902, 672) describes the history of introduction of fan; *see* also Rabe (*ibid.* 1905, 1735), and Schliebs (*ibid.* 1905, 1900).

O'Brien places a cast-iron fan immediately behind the burners before the nitre oven and Glover tower. The temperature inside the fan is 540°, and it is covered with a 1-in. coat of asbestos cement; water is used as a lubricant instead of oil (Falding, Min. Ind. ix. 621). The actual volume of gas passing through the chamber system may be determined by measuring the speed of the gaseous current in the connecting pipes or exit pipe by means of Fletcher's or Swan's anemometer.

Gay-Lussac and Glover towers. In 1827 Gay-Lussac proposed the use of a coke tower for absorbing the escaping nitrous fumes in strong sulphuric acid, but it was not until 1842 that the idea was put into practice, and it was not until some time after the invention of the Glover tower in 1860 that the Gay-Lussac came into general use. This delay was due to the fact that up to that date, all the acid used in the latter tower had to be concentrated, and the nitrous vitriol obtained could only be denitrated by dilution with water, so that the saving in nitre was partly counterbalanced by the cost of the fuel required for reconcentrating the acid. But the introduction of the Glover tower rendered this expense unnecessary, and at the present day there are very few sulphuric acid manufacturers who do not make use of these appliances.

The Gay-Lussac tower consists of a tall column, the walls of which are of lead, packed with some material, such as coke, which presents a large surface so as to bring the gas passing up through the tower into intimate contact with a stream of sulphuric acid entering at the top and passing down the tower. It is connected with the exit from the last chamber of a set, and receives all the gas leaving that chamber; this gas contains a large amount of nitrous vapours, which are absorbed by the descending sulphuric acid and again introduced into the process.

The tower is usually built on a solid block of brickwork or on strong brick piers, surmounted by an arch, or cast-iron columns may be employed, carrying a platform of iron bearers or rails. The brickwork or iron is protected from possible acid drops or leaks by sheet lead. The tower itself is constructed of sheet lead, supported by a wooden frame-work in the same manner as the chambers. Sometimes angle iron is used instead of timber for the frame. Square-sectioned towers are usually preferred, as being somewhat simpler to construct than round ones, but the latter have the advantage that for a given capacity less lead is required, and the gaseous current is more uniformly distributed within the tower. The sides are usually made of 8 or 10 lb. lead, and the bottom, which is turned up at the edges to form the upstand, of 12–18 lb. lead. The sides are not 'burnt' to the bottom, but dip into the acid, which forms a lute as in the chambers. The lower portion is usually lined with acid-proof blue bricks, put in dry without mortar or cement in order to protect the lead from being damaged by the packing. 1-in. splits are sometimes used to economise space.

The width varies from 4 to 10 ft., and the height from 30 to 50 ft., the dimensions depending on the capacity of the set of chambers.

The cubical contents should be at least equal to 1 p.c. of the chamber space, and may with advantage be increased to 2 p.c. when working with a normal chamber capacity of 16–20 cb. ft. per lb. of sulphur burnt per 24 hours. But when the chamber space is reduced to 10 or 11 cb. ft. per lb. sulphur, as in intensive working, the capacity of the Gay-Lussac tower is frequently increased to about 4 p.c. of the total capacity of the chambers. Two towers are usually employed in this case, and also with large sets in non-intensive working.

Sometimes the gases from a number of different sets of chambers, after leaving the Gay-Lussac towers, are passed through a large final absorbing tower in order to reduce the loss of nitrous vapours due to non-absorption to a minimum.

The pipe bringing the gases from the last chamber enters the side of the tower near the bottom, and just above is fixed the grating which carries the packing. This grating may consist of iron bars covered with lead, carried by the brick lining, or it may be of blue bricks on a series of parallel brick arches or of specially shaped acid-proof stoneware blocks. The packing itself used at one time almost universally to consist of hard-burnt furnace coke, and the latter is still used to a very considerable extent, but owing to the fact that it is apt to disintegrate in the tower which it gradually blocks, and that it also has a slight reducing action on the higher oxides of nitrogen, it has been, to a certain extent, replaced by cylinders of acid-proof stoneware, specially-shaped bricks, Guttmann stoneware balls, or Bettenhausen cones. When coke is used large lumps 12 or 14 ins. long are placed on the grating in regular layers, and the size of the fragments is gradually reduced as the packing goes on, until in the upper part pieces 3–4 ins. in size are employed. The top of the tower consists of sheet lead supported from above by iron bars covered with lead, and a large number of inlet holes for the acid are spaced over the whole area. Each hole has an upstanding rim, which is covered with a leaden cap which allows the acid to pass into the tower, but no gas to escape. The acid is conveyed to these lutes by leaden pipes from the bottom of a leaden box divided by radial partitions into sections which are continuously fed with acid by means of a reaction wheel or rotating distributor working on the principle of the Barker's mill. Another method of distribution is by means of an intermittent siphon, which at regular intervals flushes an intermediate leaden box from the bottom of which numerous pipes run to the lutes. The reaction wheel or siphon is fed with acid from an overhead tank, and the quantity passing down the tower is regulated by a tap. As it is of the utmost importance to the working of the process that this stream should be as uniform as possible, and since any variations in the level of the acid in the tank above will cause similar variations in the quantity the regulating tap will pass, various contrivances are employed for ensuring a uniform pressure of acid at the point of delivery. The most efficient of these is the balancing apparatus described by Lunge (Sulphuric Acid, vol. i. 599), in which the acid flows from the bottom of the tank into a smaller intermediate vessel on the same level in which a hollow leaden ball is suspended from the end of a lever. The entering acid presses the ball upwards, the other end of the lever descends and closes the outlet from the tank until sufficient acid has run out of the intermediate vessel to allow the ball to move down and open the outlet valve again. Thus the level of the acid in the small vessel will be independent of that in the main tank.

The acid is usually forced up to the top of the tower by means of compressed air from a strong cast-iron vessel which is sometimes lined with lead, but this is unnecessary, as acid of the strength used has very little action on cast iron. These acid eggs, as they are called, hold several tons of acid. Latterly they have been replaced in some works by automatic elevators or pulsometers, which were first introduced by Harrison Blair, and have been considerably improved by Laurent and Kestner. They work continuously, and the rate of supply of acid to the towers can be regulated by the air-inlet cock below, so that no regulating arrangement or large storage tank is required on the top. When the tower is very high and the air pressure available is not sufficient to force the acid up to the top in a continuous stream, a modification of the automatic elevator, known as an *Emulseur*, may be employed, in which a certain amount of air is allowed to mix with the acid as it is forced up, the emulsion of acid and air requiring less pressure to elevate it than the acid by itself.

T. Meyer (Zeitsch. angew. Chem. 1910, 972) recommends the use of multistage turbine centrifugal pumps of hard lead connected to an electric motor, which he states have an efficiency of 19·4 p.c. of the total energy supplied as against 3½ p.c. when compressed air is used.

Working the Gay-Lussac tower. The acid used for absorption should be at least 144°Tw., and it will be more efficient if it is 150°–152°Tw.; it may readily be obtained of the latter strength from the Glover tower. It should also be as cool as possible, not above 30°C. Hot acid absorbs badly, and where coke is used for packing some of the higher nitrogen oxides may be reduced to nitric oxide. The quantity used per 24 hours should be at least equal to one-half the daily production of acid, and in many cases a quantity equal to the total daily make is used; in intensive working at least twice the daily production has to pass through the Gay-Lussac towers in order to prevent excessive loss of nitre.

The nitrous vitriol running off from the bottom of the tower usually contains from 1 to 2 p.c. N_2O_3; it is a solution of nitrosulphonic acid or nitrososulphuric acid (chamber crystals) $SO_2(OH)(NO_2)$ in sulphuric acid, and it is decomposed on dilution with water, the N_2O_3 being liberated. The percentage of N_2O_3 depends on the quantity of acid run down the tower; if it contains above 2 p.c. N_2O_3 there is danger of loss from incomplete absorption. When the process is working regularly it is almost colourless, but when the exit gases contain an excessive amount of unoxidised SO_2 it turns dark purple owing to the reduction of the $SO_2(OH)(NO_2)$ to $SO_2(OH)N(OH)O$, called by Raschig nitrosisulphonic acid, and appears full of bubbles of NO. It has been stated that some nitric acid is usually present in the nitrous vitriol, but Lunge holds that this is never the case under normal conditions of working. If such an excess of nitre be used that N_2O_4 exists in the gases leaving the last chamber, some nitric acid will probably be formed, but if the tower is packed with coke the latter will prevent this formation, and only where some non-reducing packing is employed is it likely that the formation of nitric acid will take place (J. Soc. Chem. Ind. 1885, 31). Lunge also controverts the statements of Benker and Lasne that when sulphur dioxide is practically absent from the gases entering the Gay-Lussac tower, the N_2O_4 present is not readily absorbed by the acid in the tower. To avoid this loss they proposed to introduce into the gases leaving the last chamber, a certain quantity of burner gas by means of a steam jet in order to reduce the N_2O_4 to N_2O_3, which is more readily absorbed (D. R. P. 17154, 1881). Benker modified this at a later date (D. R. PP. 88368, 91260) by taking a small quantity of gas from the first chamber and injecting it into the last or into a special chamber between this and the Gay-Lussac tower.

Petersen (D. R. P. 226793, 1909) states that ferrous sulphate in the Glover tower acid hinders the absorption of nitrous acid in the Gay-Lussac tower, and recommends that the ferrous sulphate should be oxidised by the addition of a little nitrous vitriol to the absorbing acid for the last tower.

The quantity of N_2O_3 in the nitrous vitriol may be estimated by means of potassium permanganate. 50 c.c. of N/2 $KMnO_4$ solution are taken, diluted with five times the volume of water, and the nitrous vitriol is run in from a burette with constant stirring until the colour just vanishes. 1 c.c. N/2 $KMnO_4$=0·0095 grms. N_2O_3.

If nitric acid is present it is not estimated by this method, but the total nitrogen compounds present may be determined by means of Lunge's nitrometer, in which they are converted into NO by shaking with mercury and the volume of gas produced can be measured. The following table represents the quantities of various nitrogen compounds in milligrams corresponding with 1 c.c. of NO at 0°C. and 760 mm.

NO	N	NO	N_2O_3	N_2O_5	HNO_3	KNO_3	$NaNO_3$
1 c.c. . .	0·627	1·343	1·701	2·417	2·820	4·521	3·805
2 ,, . .	1·254	2·686	3·402	4·834	5·640	9·042	7·610
3 ,, . .	1·881	4·029	5·103	7·251	8·460	13·563	11·415
4 ,, . .	2·508	5·372	6·804	9·668	11·280	18·084	15·220
5 ,, . .	3·135	6·715	8·505	12·085	14·100	22·605	19·025
6 ,, . .	3·762	8·058	10·206	14·502	16·920	27·126	22·830
7 ,, . .	4·389	9·401	11·907	16·919	19·740	31·647	26·635
8 ,, . .	5·016	10·744	13·608	19·336	22·560	36·168	30·440
9 ,, . .	5·643	12·087	15·309	21·753	25·380	40·689	34·245

The Glover tower. Before the invention of the Glover tower the methods used for decomposing the nitrous vitriol obtained from the Gay-Lussac tower in order to reintroduce the nitrous compounds into the process were dependent on the use of hot water or steam, or else sulphur dioxide, dilution of the acid being necessary in both cases. The wear and tear of the apparatus employed was always very considerable, and as only dilute acid was obtained, additional expense was incurred in concentrating the acid again for supplying the Gay-Lussac tower. This was sometimes done by means of evaporating pans placed on top of the pyrites, or sulphur burners, but owing to danger of leakages this method did not come into general use. The advantages of the use of the Glover tower over any other system of denitration are that the heat of the burner gases is utilised for restoring the nitrous vapours uniformly to the chambers, and also for supplying them with steam, and that the burner gas is cooled down to such a temperature that no cooling pipes are required, and the wear and tear on the first chamber is considerably reduced.

Owing to the higher temperature of the gases Glover towers (Fig. 7) must be far more strongly built than Gay-Lussac towers, which in other respects they greatly resemble. The sides are usually of 14–18 lb. lead, and the bottom of 35 lb. lead, and the tower is lined with firebricks capable of resisting both heat and strong acid, or with volvic lava; this lining, which is put in dry without mortar of any kind, is about 2 ft.

3 ins. thick at the bottom, and decreases from 18 ins. above the grating carrying the packing to 4½ ins. at the top. The packing usually consists of flint, picked from the chalk, and washed with hydrochloric acid. This material has the advantage of being absolutely acid resisting, but it is very heavy, does not possess much surface, and is readily blocked up by dust. Acid-proof fireclay cylinders or bricks, either plain or dished and perforated, are frequently used instead, more particularly where pyrites dust burners are employed. They do not block up so readily, and also allow more free space in the tower for the reactions (Lüty, Zeitsch. angew. Chem. 1896, 645). Sometimes coke is used in the upper portion, but there is always danger of the coke firing should the acid feed be stopped for any reason. In America Herreshoff uses a particular kind of quartz rock, not only for the packing itself, but also for the grating supporting the packing, and for the lining; as the lumps of quartz are not obtained in very regular shape the space next the lead is packed with a thick layer of quartz sand; the lead is protected outside by iron plates (J. Soc. Chem. Ind. 1908, 269).

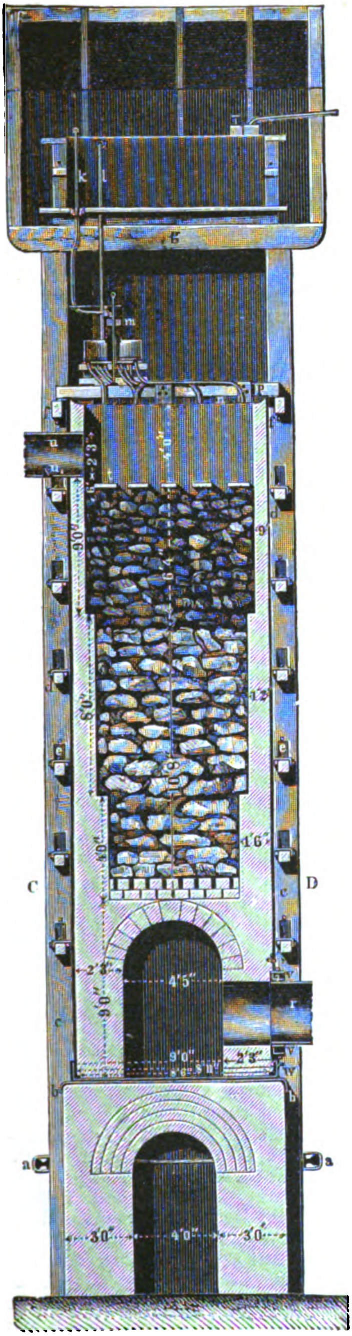


Fig. 7.

Volvic lava is largely used on the Continent both for lining and for packing Glover towers. In some cases the tower itself is made of this material without any leaden shell. The segments are held together by iron hoops covered with lead. There are no tanks on the top, as the tower is fed by means of automatic elevators from below.

The height of the Glover tower is generally much less than that of the Gay-Lussac tower, from 20 to 30 ft., while the width is proportionately greater, so that the cubic capacities of the two do not widely differ. A tower 9–10 ft. square and 25–30 ft. high containing 2025–3000 cb. ft. will suffice for a set of chambers containing 140,000–200,000 cb. ft. From 550 to 600 cb. ft. per ton of sulphur burnt daily is a proportion frequently employed; these figures refer to the total cubic capacity inside the lead, the actual working space being only about one-half this amount.

The gases enter the tower from the burners usually by a cast-iron pipe, and pass upwards through a grating of fireclay slabs or groined arches which carries the packing. Niedenführ recommends the construction of a second arch and grating a little higher up the tower so that the lower portion may be cleaned or replaced without disturbing the main body of the packing (Lüty, Zeitsch. angew. Chem. 1905, 1253). At the top similar arrangements are employed for distributing the acid as in the Gay-Lussac tower. There are two storage tanks on the top, one containing nitrous vitriol and the other chamber acid, and the two streams usually mix in the distributing box before entering the tower. When the additional nitre required for the process is introduced as liquid nitric acid, it is either mixed with the nitrous vitriol in the storage tank or else run into the centre of the top of the tower in a regular stream by means of a glass tube from a Mariotte's bottle, as previously described.

The hot concentrated acid leaves the saucer below by a lip, and is cooled by passing through a leaden trough in which leaden coils or pipes are placed, through which cold water is kept running. Usually Gay-Lussac and Glover towers are built side by side, the latter standing on a higher foundation so that the tops are on the same level. The inspection and control of the two towers is thus much facilitated.

If the Glover tower is fed with nitrous vitriol alone, the latter will not be completely denitrated when it reaches the bottom, but will contain about 0·2 p.c. of N_2O_3. It is usual, therefore, to mix it with a certain amount of chamber acid of from 110° to 120°Tw. in order to produce a mixture of from 130° to 136°Tw., from which the nitrous compounds will be completely removed by the hot burner gases by the time it arrives at the bottom of the tower. If more or weaker chamber acid is used, and a mixture is obtained below 130°Tw., there is danger of loss of nitric oxide from the decomposition of the nitrous vitriol outside the tower; at the same time, instead of obtaining an acid of 150°Tw. or thereabouts, running off at the bottom, the latter may only be 140°Tw., at which strength it is not nearly so efficient for absorbing the nitrous vapours in the Gay-Lussac tower. It is possible, by keeping the acid in the chambers up to at least 120°Tw., to pass the whole of the chamber acid made down the Glover tower with the nitrous vitriol, to completely denitrate the latter and to obtain the whole of this acid at 145°–150°Tw.

The temperature of the burner gas leaving the pyrites kilns will be about 500°C., and if there is no dust chamber employed the gas will enter the Glover tower at from 400° to 450°C., and will leave it at between 50° and 80°C. A dust chamber will probably cool the gas another 100°C. before it enters the tower; it will then not be possible to concentrate so much chamber acid in the latter, but perfect denitration can be obtained, the acid running off at the bottom being 140°–148°Tw. Niedenführ recommends the dividing of the Glover function between two apparatus; after the dust chamber comes a concentrating tower, then a hard lead fan, and then the denitrating tower. Acid of 130°Tw. leaving the second tower is concentrated to 142°Tw. in the first (Lüty, Zeitsch. angew. Chem. 1905, 1253).

Petersen, in order to deal with the large amount of absorbing acid used in working on the intensive system, also recommends the use of two Glover towers, together with two Gay-Lussac towers, the first Glover and the last Gay-Lussac towers working together with acid of 1·7 sp.gr., whilst for the inner towers 1·6–1·65 acid is employed (Zeitsch. angew. Chem. 1907, 1101).

In other cases, where there are several sets of chambers each working with a single Glover tower, some are worked to make strong acid (which need not be denitrated completely) for the Gay-Lussac towers, while the others produce a larger quantity of a weaker acid quite free from nitrous compounds and ready for sale or use.

Where two towers are employed in series the first removes many impurities from the gases, so that the acid concentrated in the second is much purer than that running from the first.

The concentration of the acid in the Glover tower is not due solely to the evaporation of water; it is also very largely due to the production of sulphuric acid in the tower itself, partly from the sulphur trioxide in the burner gas, and partly from oxidation of sulphur dioxide by the nitrous vitriol. Scheurer Kestner found by actual measurement that 17–19 p.c. of the total acid made was produced in the Glover tower, of which about 3·5 p.c. was due to sulphur trioxide in the gases (Bull. Soc. chim. [ii.] 44, 98).

Meyer (Zeitsch. angew. Chem. 1909, 1841) obtained in two cases only 10·8 and 7·3 p.c. of the total make; and Raschig, by estimating the sulphur dioxide in the gases entering and leaving the tower, found that about 14–16 p.c. of the daily production was formed there. Sorel (Bull. Soc. Ind. Mulhouse, 1889, 240; also J. Soc. Chem. Ind. 1890, 175) explains this formation in the following way: The nitrous vitriol is denitrated in the lower part of the tower, and some of the nitric oxide liberated is oxidised as it ascends, and is reabsorbed by the fresh acid entering at the top and brought down again to be once more denitrated by the sulphur dioxide. In this way a comparatively small amount of nitrogen oxides converts a comparatively large amount of sulphur dioxide into sulphuric acid in the same way as in the chambers subsequently, except that in the tower, the reactions are intensified by the constant subdivision and mixing of the gases, and the contact with a large amount of surface wetted with nitrous vitriol. The heat developed by the intensive reactions in the tower is expended again in evaporating water from the weak entering acid. If the top part of the tower gets too cold, either through the tower being too high or from the large amount of weak acid entering, the denitration will take place in a comparatively small zone near the top, and less acid formation will take place in the tower. Lunge calculates that with 250 cb. ft. of active Glover tower space per ton of sulphur, and a chamber space of 20 cb. ft. per lb. of sulphur burnt per 24 hours, if $\frac{1}{8}$ of the oxidation takes place in the tower and $\frac{7}{8}$ in the chambers, the denitrating zone of the Glover tower makes 224 times more acid than an equal cube of chamber space (Sulphuric Acid, vol. i. 671).

THE CHAMBER PROCESS.

Before starting a set of chambers the saucer should be luted with acid of at least 90°–100°Tw.; if the sides are 'burnt' to the bottom this is not necessary; but water must on no account be used, as it will dissolve the nitrous vapours with the formation of nitric acid which will rapidly attack the lead of the chamber bottom. The dampers are then opened at the end of the system and before the Glover tower, a stream of acid is started running down the latter, the kilns are charged and the hot burner gases are allowed to enter; at the same time three or four times the quantity of nitre required for normal working is charged in the nitre oven or introduced as liquid nitric acid in the Glover tower. As soon as the drips show that sulphuric acid is condensing in the chambers steam is introduced, the quantity admitted being regulated from time to time according to the strength of the drips. Excess of nitre is used until the gas in the last chamber shows a reddish-yellow colour, when the acid feed on the Gay-Lussac tower is started, and as the nitrous vitriol from the latter becomes available for use in the Glover tower, the quantity of fresh nitre is reduced until the minimum required for the regular working of the process is reached.

The strength of the chamber acid. In England the acid in the first chamber is generally kept at from 120° to 125°Tw., and the steam or water admitted is regulated by the strength of the drips, which usually are 5°–10°Tw. higher than the bottom acid. If the strength exceeds 125°Tw. the quantity of nitrous fumes dissolved in the acid begins to increase very considerably, and the wear and tear of the chamber through corrosion of the lead is notably increased. On the Continent it is more usual to keep the first chamber weaker, from 106° to 110°Tw. The subsequent chambers are all worked a little weaker than the first, the last chamber being usually kept at from 90° to 100°Tw., except in the now very exceptional case where there is no Guy-Lussac tower, when it is reduced to 50°–60°Tw.

The colour of the gases in the chambers requires continuous inspection in order to see if the correct amount of nitre is being used. For this purpose glass windows are let into the sides of the chambers and into the exit pipes from them, the gas being viewed either horizontally through opposite windows or diagonally upwards towards a light in the roof consisting of a bell-jar placed in a hydraulic lute. The first chamber, owing to the fact that it is full of sulphuric acid mist, will not show any decided colour, but the following chambers should appear distinctly reddish-yellow, the colour gradually deepening till in the last chamber it is dark-red, and even in the exit pipe to the Gay-Lussac it shows a decided colour. The smaller the chamber space employed the deeper this colour will have to be in order to prevent the escape of unoxidised sulphur dioxide, and also nitric oxide with the exit gases from the Gay-Lussac tower. After the latter the gases should show no colour whatever; if they do show a yellowish tint it means that an excess of nitre is being used in the process, or else that the absorbing capacity of the Gay-Lussac tower is insufficient for the nitrous gases present.

Whenever the gases in the last chamber are pale in colour it means that something is wrong; it may be due simply to a shortage of nitre, or it may be caused by too little or too much steam being present; if too little steam is being used the condensing acid will be too strong and will contain much nitrous acid, whilst if too much is being introduced the condensing acid will be weak and will contain nitric acid. Another cause of pale gases is shortage of oxygen due to insufficient draught; analysis of the burner gas or a determination of the percentage of oxygen in the exit gas will at once show whether this is the cause or not. Whatever may be the cause, pale chamber gases mean unoxidised sulphur dioxide and an excess of nitric oxide in the gases entering the Gay-Lussac tower, and as the acid running down the latter will not absorb either of these gases they pass away and are lost. In any case, extra nitre must be introduced at once into the process to replace this loss, and the cause of the disturbance determined and corrected as soon as possible. If too much nitre is being employed the acid condensing in the chambers and in the drips will show the presence of an excessive amount of nitrous acid if tested with ferrous sulphate solution. The bottom acid in the first chamber should give no coloration by this test, and the drip acid only a faint indication. The middle chambers should not give more than a faint indication in the bottom acid and a stronger one in the drips. The last chamber usually gives a decided reaction in the bottom acid and a strong one in the drips.

The regular observation of *the temperatures of the gases* in the chambers by means of thermometers with their bulbs several inches inside the walls is very useful in controlling the working of the process. These temperatures depend chiefly on the intensity of the reactions taking place in the chambers; if the outside atmospheric conditions do not vary much, they should be fairly constant when the process is working well. The loss of heat by radiation will vary according to the external temperature, the force of the wind, &c., more particularly when the chambers are not enclosed in buildings, but the differences between the temperatures of the chambers and the external air should not vary much. The first chamber will be the hottest, and the last the coolest, and different parts of the same chamber will show slight variations, the upper part being a little warmer than the bottom, and the exit cooler than the entrance. There is considerable difference of opinion as to the best temperature for the chamber process. With moderate chamber space the first chamber should not exceed 60°–70°C., the later chambers being, of course, cooler, the last showing a reading of 25°–35°C. In intensive working with only 11 or 12 cb. ft. chamber space the temperatures will be some 20° higher unless means are taken to obtain additional cooling of the gases to that due solely to radiation from the chamber walls. These high temperatures certainly mean additional corrosion, and wear and tear of the lead, and in all probability increased destruction of the available oxides of nitrogen by secondary reactions giving rise to the formation of nitrous oxide and nitrogen. With regard to the lower limit of temperature there is some difference of opinion. Meyer (Zeitsch. angew. Chem. 1901, 1245) states that the temperature for best working is probably above 50°C., but Lunge is of opinion that the process always works better and with a greater economy of nitre in cold weather than in hot, provided that the temperature does not fall so low that ice is formed in the chambers. On the other hand, since the introduction of water sprays instead of steam, experience seems to show that in very cold weather some steam has to be used, more particularly in the back chambers, in order to obtain the best results.

The pressure of the gases in the different chambers will not be uniform throughout; where only natural draught is employed there is usually a slight outward pressure in the first chamber, in the intermediate chambers the gas is practically in equilibrium with the outside air, while in the last there is a slight suction. These pressures are regulated by means of the dampers between the burners and the chambers, and at the end of the system; where no chimney is employed, and the production of the draught depends chiefly on the upward pressure of the hot gas column between the burners and the Glover tower there is frequently a pressure right through the system, gradually decreasing from first to last.

Where mechanical draught is employed the pressures will depend on the position of the fan. Niedenfuhr recommends working with a considerable pressure throughout the chambers by placing the fan between two Glover towers and throttling the gas behind the Gay-Lussac tower (Lüty, Zeitsch. angew. Chem. 1905, 1253). But fans are usually placed at the end of the system where they may produce a considerable suction in the chambers. In any case, the draught must be so regulated that the oxygen in the exit gases is not less than 5 p.c., nor greater than 8 p.c. Between these limits opinions differ as to what the excess should be, 6 p.c. being perhaps the most generally accepted figure.

The total quantity of nitre required depends chiefly on the chamber space. Working with pyrites and a chamber space of 24 cb. ft. per lb. of sulphur burnt per 24 hours, this will amount to about 10 p.c. on the sulphur. With less chamber space 15–20 p.c. nitre will be required, whilst for intensive work and a chamber space of 11 or 12 cb. ft. as much as 25 p.c. nitre will probably have to be used. The amount of fresh nitre to be introduced will depend chiefly on the quantity recovered in the nitrous vitriol from the Gay-Lussac tower, and will therefore vary with the efficiency of that apparatus. Generally 3–4 p.c. of fresh nitre has to be used with moderate tower capacity and chamber space; even where the absorbing capacity of the Gay-Lussac tower is very large, the quantity required is never less than 2 p.c., whilst any irregularity in the working of the process may cause a much greater loss of nitre from defective absorption, a correspondingly greater quantity of fresh nitre being required to replace this loss.

Widely different views have been held by different experimenters as to the relative functions of different parts of the same chamber —*i.e.* the lower middle and upper zones, and the portions adjoining the sides and top as compared with the interior.

Mactear (J. Soc. Chem. Ind. 1884, 228), as the result of a series of experiments in which the acid condensing in different parts of the chamber was collected by a number of trays each 1 ft. square, came to the conclusion that most chemical action takes place in the upper part of the chamber, and least near the bottom. Lunge and Naef (J. Soc. Chem. Ind. 1884, 663), on the other hand, deduced from their experiments that the acid formation is greatest near the top, bottom, and sides, and least in the central portion, while Hasenclever concluded that the acid condensed is practically the same per given amount of space in all parts of the interior of a given chamber. There is no doubt that the cooling influence of the external air, together with the surface action of the walls and top, cause a greater condensation of liquid acid along the roof and sides, and Lunge's and Naef's analyses appear to show that there is always more sulphur dioxide in the central part of the chamber than near the outside, pointing to a stronger formation of acid near the chamber walls. They also give a certain amount of support to Abrahams' theory concerning the path taken by the gases within the chambers (Dingl. poly. J. 1882, 416). He is of opinion that the cooling action of the walls and top causes the gas to rise in the centre of the longitudinal section and to descend along the sides of the chamber; so that the gases travel in vertical layers at right angles to the length of the chamber, from front to back, but each single gaseous molecule describes a spiral line, whose axis is parallel to the length of the chamber.

Lunge and Naef have also shown that the conversion of sulphur dioxide into sulphuric acid goes on rapidly in the first half of the first chamber, then slackens very much, but is suddenly revived when the gases pass into the next chamber. This has been confirmed by Schertel (Chem. Ind. 1889, 80), Retter (Zeitsch. angew. Chem. 1891, 4), and others, and is due partly to the better mixing of the gases in passing through the connecting pipe and partly to the cooling and condensing effect of the latter.

The relative amounts of acid formed in a series of chambers have been stated by Hurter (J. Soc. Chem. Ind. 1882, 8) to decrease approximately in geometric progression from the first chamber to the last. Thus with a series of four chambers of equal size, if $\frac{2}{3}$ of the production takes place in the first, $\frac{2}{9}$ will be formed in the second, $\frac{2}{27}$ in the third, and $\frac{2}{81}$ in the fourth. Lunge and Naef have shown that this is only approximately correct.

The examination of the exit gases passing away from the Gay-Lussac tower is a most important part of the control operations requisite for carrying on the process efficiently. Samples may be taken at intervals during each day, or an average sample may be drawn every 24 hours by aspirating a slow stream at a definite rate through a series of absorption bottles containing caustic soda in order to absorb the acid gases. According to the Alkali Works Regulation Act, in England the total quantity of sulphur acids escaping from the exits of sulphuric acid works must not exceed 4 grns. per cb. ft. calculated as sulphur trioxide. This is usually determined by shaking a definite volume of the gas, taken by means of a flexible bellows aspirator, with a solution of hydrogen peroxide and titrating with standard caustic soda solution, using methyl orange as indicator. According to the Alkali Works Inspectors' reports the average acid escapes in England during 1908, 1909 and 1910 were 1·163, 1·162, and 1·178 grains SO_3 per cb. ft. But this test takes no account of the oxides of nitrogen escaping with the gases. Hurter and Lunge (Alkali Makers' Handbook, 98) recommend the following arrangements for estimating the different acids in the exit gases. These agree in the main with those published by the British Alkali-Makers Association in 1878. About 24 cb. ft. of the gases are drawn in 24 hours through four absorption bottles, the first three containing normal caustic soda solution, and the fourth distilled water. The contents are mixed together and divided into three equal parts. One is tested with normal sulphuric acid solution to determine the total acidity. The second is poured into a warm solution of potassium permanganate, strongly acidified with sulphuric acid to oxidise all the nitrogen acids to nitric acid, any considerable excess of permanganate being reduced by sulphur dioxide solution until the colour is a faint pink. It is next mixed in a flask with 25 c.c. of a solution of ferrous sulphate (containing 100 grms. $FeSO_4,7H_2O$ and 100 grms. H_2SO_4 per litre), to which 20–25 c.c. H_2SO_4 has been also added, all air being first expelled by a current of carbon dioxide. The flask is boiled to expel nitric oxide, and the solution is of a light yellow colour, and the unoxidised ferrous sulphate is determined by titrating with N/2 permanganate solution. If V be the volume of air aspirated after reduction to 0°C. and 760 mm., x the number of c.c. of normal sulphuric acid used in the first titration, y that of the permanganate used during the second test, and z the quantity of permanganate equivalent to the 25 c.c. iron solution, then the

Grms. per cubic metre

$$\text{Total acidity } SO_3 = \frac{0{\cdot}12(100-x)}{V}$$

$$\text{Sulphur } S = \frac{0{\cdot}008(600-6x-z+y)}{V}$$

$$\text{Nitrogen } N = \frac{0{\cdot}007(z-y)}{V}$$

Grains per cubic foot

$$\text{Total acidity } SO_3 = \frac{1{\cdot}852(100-x)}{V}$$

$$\text{Sulphur } S = \frac{0{\cdot}12346(600-6x-z+y)}{V}$$

$$\text{Nitrogen } N = \frac{0{\cdot}10803(z-y)}{V}$$

Nitric oxide is estimated by passing the gases after leaving the first four bottles through a tube containing 30 c.c. N/2 permanganate and 1 c.c. sulphuric acid, sp.gr. 1·25. Excess of standard ferrous sulphate solution is added, and the excess is titrated back by N/2 permanganate solution. Then the nitrogen present as—

$$NO = \frac{0{\cdot}007 \times A}{3V} \text{ grms. per cubic metre}$$

$$= \frac{0{\cdot}10803 \times A}{3V} \text{ grains per cubic foot}$$

where A = number of c.c. of N/2 permanganate reduced by the NO.

Fig. 8 shows the best form of absorbing apparatus for estimating the nitric oxide according to Lunge.

The oxygen is determined in the residual gas after the acid gases have been all removed.

Carpenter and Linder (J. Soc. Chem. Ind. 1902, 1490) have investigated the methods employed for estimating the acidity of the gases escaping from the chamber process, and find that when soda is used to absorb the acid gases reactions arise with formation of condensation products or sulphazotised bodies whose titre is less than that of the constituents separately, and recommend the use of neutral or alkaline hydrogen peroxide for this purpose.

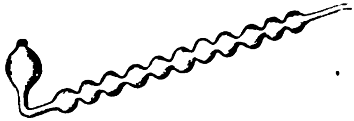


FIG. 8.

Proposals for diminishing chamber space. A number of proposals have been made from time to time for the purpose of increasing the rapidity of the acid formation in the chambers, and thereby reducing the chamber space necessary for the production of a definite quantity of acid.

Additional surface has been provided by means of lead partitions in the chambers, but these quickly corrode, while partitions of glass soon collapse. Walter and Boenig (Eng. Pat. 14944, 1891) employ double walls of acid-proof material arranged across the whole width of the chambers; the main portion of the gas has to traverse the spaces between these, entering at the bottom and leaving at the top, while the remainder passes through numerous small holes in these partitions.

Richter (D. R. P. 15252) aspirates the gases from the lower part of the chamber and introduces them again near the top, and Boult (Eng. Pat. 10757, 1899) brings the gases back from the rear of the apparatus to the front again to obtain a better admixture and circulation.

Rabe (Zeitsch. angew. Chem. 1910, 8 and 1115) suggests methods to facilitate the circulation of gases in rectangular chambers spirally (Abraham's theory) by introducing the gases in the direction of the Abraham currents, by gradually reducing the height of the chamber from front to back or by introducing lead curtains hanging down at intervals a certain distance from the roof, parallel with the ends of the chamber, or the introduction of acid sprays in the direction of the currents. He also criticises Porter's experiments with regard to the movements of the gases in the chambers.

But mixing the gases alone is not sufficient, and arrangements for this purpose have not had any great success. Hartmann (Chem. Zeit. 1897, 877) employs a number of shafts 5 or 6 ft. wide from top to bottom of the chamber, luted at the bottom so that a continuous current of cooling air passes up them, and states that he has obtained an increased production of 20 p.c. by this means. Meyer (Zeitsch. angew. Chem. 1900, 74; 1901, 1245) has introduced into the first of his circular chambers a system of cooling pipes, reaching down into the chamber about 8 or 10 ft., and cooled by water which enters the pipes by means of narrower ones reaching nearly to the bottom of the wider ones. By this means he removes 15–20 p.c. of the heat of the reaction, and obtains a corresponding increase in the production. The greatest success, however, in increasing the output of vitriol has been obtained by the employment of mixing and cooling towers between the chambers. Lunge (Zeitsch. angew. Chem. 1899, 385; J. Soc. Chem. Ind. 1889, 774) was the first to introduce these successfully; his plate towers consist of columns of perforated stoneware plates contained in a lead-lined tower into which the gases enter at the bottom and leave at the top. They are fed with a stream of water or dilute sulphuric acid at such a rate that by the vaporisation of water the temperature does not rise above 70° or 80°C. Fig. 9 shows a Lunge tower packed with plates, and Figs. 10 and 11 represent the plates in sectional elevation and plan, from which it will be seen that there is always a thin layer of liquid on each plate, and they are so arranged that the openings in consecutive layers are not in the same vertical line. By this means a very intimate contact between the gas and liquid is obtained. According to Lunge, these towers do from 10 to 20 times as much work as an ordinary coke-packed Gay-Lussac tower of the same cubic capacity, in place of which they are sometimes used. But it is as intermediate towers between the chambers that they are mostly employed. By feeding them with acid above 1·3 sp.gr. the possible formation of nitrous oxide is avoided (Lunge, Ber. 1881, 2200). The heat of reaction in the formation of chamber acid furnishes enough heat to evaporate 100 parts of water at 100°C. during the production of 98 parts H_2SO_4, a quantity 25 p.c. in excess of the requirements of the process; but most of this excess of heat will be dissipated by radiation from the tower walls (Lunge, Sulphuric Acid, vol. i. 487). Lunge towers have come into considerable use on the Continent; their chief drawback is due to amount of obstruction of draught they cause, but where fans are employed this is easily overcome. Niedenführ (Chem. Zeit. 1896, 31; J. Soc. Chem. Ind. 1896, 541) describes a number of chamber systems where they have been introduced with very satisfactory results. *See* also Lüty (Zeitsch. angew. Chem. 1897, 484); and Niedenführ (Chem. Zeit. 1897, 20); Lütz and Niedenführ (Zeitsch. angew. Chem. 1902, 242; 1905, 1253).

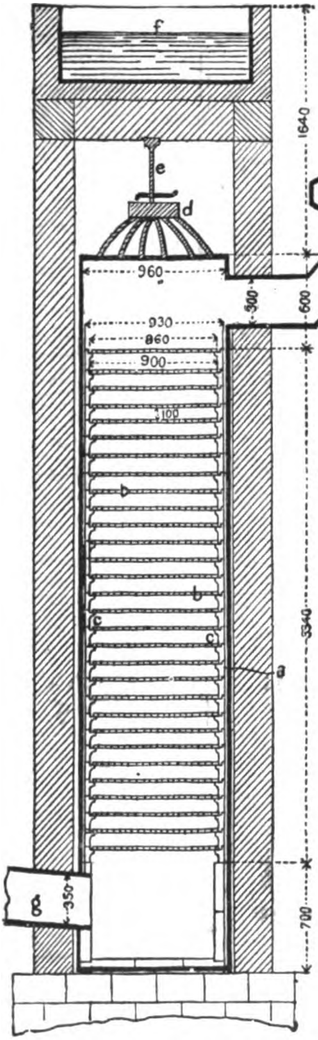


FIG. 9.

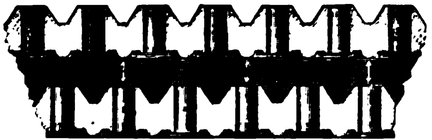


FIG. 10.

Other apparatus based on the same principle as the plate towers have been introduced by other inventors. Gilchrist (J. Soc. Chem. Ind. 1894, 1142; 1899, 461) employs pipe columns between the chambers; these are lead towers through which pass from side to side a large number of horizontal pipes cooled by drawing air through them, while the towers are fed with water or acid. Winsloe and Hart (Eng. Pat. 20142, 1901) employ vertical air-cooling pipes set in the connecting trunks between the chambers. Benker (Fr. Pat. 238872) places leaden towers between the chambers 5 ft. wide and 20–25 ft. high, filled with stoneware cylinders; they are fed with nitrous vitriol and steam enters at the bottom with the gases. Guttmann (D. R. P. 91815) recommends hollow balls for packing reaction towers. Hart and Bailey (J. Soc. Chem. Ind. 1903, 473) employ towers between the chambers also provided with vertical tubes through which cooling air passes, and the gases pass down from top to bottom. Petersen introduces an additional tower called the 'chamber-regulator' between the last chamber and the Gay-Lussac towers; nitrous vitriol of 1·6 sp.gr. is continuously circulated through this and he claims that he obtains a more regular working of the process by this means, and considerable economy in nitre consumption (Chem. Zeit. 1909, 409).

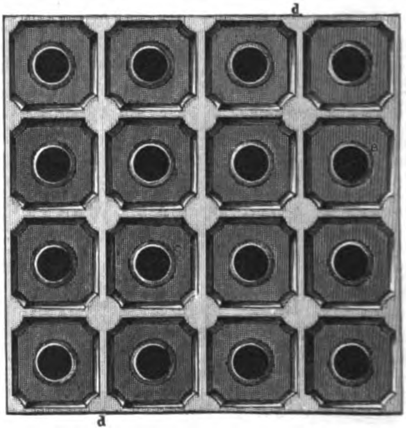


FIG. 11.

The increase in the size and number of Gay-Lussac and Glover towers, and the introduction of intermediate reaction towers, led Niedenführ (Zeitsch. angew. Chem. 1902, 242) to propose the employment of a system of towers only, without chambers, for the manufacture of sulphuric acid. Two processes have been introduced for this purpose, viz. that of Opl of Hruschau (Eng. Pat. 20171, 1908), and the

Griesheim Elektron process (Eng. Pat. 20407, 1909). Opl's process with its 8 towers in series works in a similar way to the chamber process, the nitrous vitriol from the towers 8, 7, 6, and 5 being denitrated in towers 1, 2, 3, and 4 respectively, compressed burner gases being used for elevating the acids.

At Griesheim nitric acid is used in place of nitrous vitriol, and has to be completely regenerated after the formation of sulphuric acid. But neither process has yet reached such a stage of development as to allow a definite opinion to be formed upon it (Hasenclever, J. Soc. Chem. Ind. 1911, 1292).

Hartmann (Zeitsch. angew. Chem. 1911, 2302) gives further details of the Opl process, which has now been at work four years at Hruschau. Six towers are employed like ordinary Glover and Gay-Lussac towers, and are fed by automatic elevators; the pipes leading to towers 3, 4, 5, and 6 are cooled by water; the surplus acid from 2, 3, 4, and 5 is mixed with the whole of that from 6, and finally passed through 1, which it leaves at 1·7 sp.gr. The fan is placed behind 6, and then there is a coke box to remove acid mist so that the exit acidity is only 0·22 grains SO_3 per cb. ft. 18 tons 1·7 acid are produced daily with a reaction space equal to 2 cb. ft. per lb. of sulphur burnt and a nitre consumption equal to 2·25 p.c. on the sulphur. Towers 1, 2, and 3 produce, 20, 30, and 50 p.c. of the acid, the others being simply denitrators.

THEORY OF THE CHAMBER PROCESS.

A large number of different views as to the nature of the normal chemical changes taking place in the vitriol chamber (as well as of those occurring under abnormal conditions) have been from time to time put forth by different observers. The basis on which all these views are founded is the fact that the higher oxides of nitrogen in one way or another bring about the oxidation of the sulphur dioxide in presence of water or steam to sulphuric acid, being reduced to lower oxides which take up oxygen again and then continue the cycle of changes as before.

The theories of Weber and Berzelius were very simple, and may be represented by the following equations—

(1) $3SO_2+2HNO_3+2H_2O=3H_2SO_4+2NO$.
(2) $4NO+O_2=2N_2O_3$.
(3) $2NO+O_2=N_2O_4$.
(4) $SO_2+N_2O_3+H_2O=H_2SO_4+2NO$.
(5) $2SO_2+N_2O_4+2H_2O=2H_2SO_4+2NO$.

Weber believed that equations (2) and (4) represented the chief reactions occurring, N_2O_3 or nitrous acid being the active agent, whilst Berzelius was of opinion that N_2O_4 also played an active part in the process.

The steam, oxides of nitrogen, and sulphur dioxide react, producing a fine mist of dilute sulphuric acid.

If sufficient water be not present crystals separate of the composition $SO_2(OH)(NO_2)$, a substance known as *nitrosylsulphuric acid*, *nitrososulphuric acid*, *nitrosulphonic acid*, or *chamber crystals;* but these are decomposed again into sulphuric acid and nitrous acid by excess of water or steam.

Davy and Winkler were of opinion that this substance was a temporary intermediate product in the process, and their views were represented by the following equations—

(6) $4SO_2+3N_2O_4+2H_2O=4SO_2(OH)(NO_2)+2NO$
(7) $4SO_2(OH)(NO_2)+2H_2O=4H_2SO_4+N_2O_4+2NO$
(8) $2NO+O_2=N_2O_4$.

Lunge's earlier ideas were similar only that he represented N_2O_3 as the active substance, and not NO, and his views are thus represented—

(9) $2SO_2+N_2O_3+O_2+H_2O$
$=2SO_2(OH)(ONO)$ nitrososulphuric acid.
(10) $2SO_2(OH)(ONO)+H_2O=2H_2SO_4+N_2O_3$.

By N_2O_3 here is meant the equivalent mixture of NO and NO_2. Lunge believed that this represented the chief cycle of reactions in the process, but stated that they must be modified in the first part of the chambers where there is present a large excess of NO above the proportion $NO+NO_2$. Here the following reactions may take place—

(11) $SO_2+N_2O_3+H_2O=H_2SO_4+2NO$.
(12) $2SO_2+2NO+3O+H_2O=2SO_2(OH)(ONO)$.
(13) $2SO_2(OH)(ONO)+SO_2+2H_2O$
$=3H_2SO_4+2NO$.

The last reaction represents what takes place in the Glover tower, the conditions being identical in both cases.

During the last few years a number of different views have been put forward by Lunge, Raschig, Divers, Wentzki, and others, of the reactions taking place in the chambers, which differ from each other chiefly in conceptions as to the nature of the intermediate substance or substances which are formed by the interaction of sulphur dioxide, the oxides of nitrogen and water, and which afterwards split up, yielding sulphuric acid and a lower oxide of nitrogen.

Lunge's latest ideas are given in an article published by him in conjunction with Berl (Zeitsch. angew. Chem. 1906, 19, 807–819, 857–869, 881–894). The following equations represent these—

(1) $SO_2+NO_2+H_2O=O:N(OH)SO_3H$ (Raschig's nitrosisulphonic acid or Trautz blue compound).

(2*a*) $2ON(OH)SO_3H+O=H_2O+2ONOSO_3H$ nitrososulphuric acid.

(2*b*) $2ON(OH)SO_3H+NO_2$
$=NO+H_2O+2ONOSO_3H$ nitrososulphuric acid.

(3*a*) $2ONOSO_3H+H_2O$
$=2SO_2(OH)_2+NO+NO_2$.

(3*b*) $2ONOSO_3H+SO_2+2H_2O$
$=H_2SO_4+ON(OH)SO_3H$.

(3*c*) $ON(OH)SO_3H=NO+H_2SO_4$.

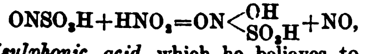
(4) $2NO+O_2=N_2O_4$.

Equations (1), (2*a*), and (3*a*) represent the chief cycle of reactions which takes place, whilst (1), (2*b*), (3*b*), (3*c*), and (4) most likely represent the reactions occurring in the first chamber where there is an excess of sulphur dioxide and much nitric oxide.

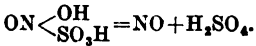
Raschig's theory of the nature of the changes by which sulphur dioxide passes into sulphuric acid was first published in 1887 (Annalen, 1887, 241, 161), but it has been several times considerably modified since then. His latest ideas were published in Zeitsch. angew. Chem. 1907, 20, 694, and further elaborated and explained in a paper read before the Society of Chemical Industry in 1911 (J. Soc. Chem. Ind. 1911, 4, 166).

He represents the following reactions as taking place—

(1) $HNO_2+SO_2=ONSO_2H$, *nitrososulphonic acid*, a purely hypothetical substance which has not been isolated.

(2) 
$ONSO_2H+HNO_2=ON<^{OH}_{SO_3H}+NO$,

nitrosisulphonic acid, which he believes to be identical with the blue compound formed when excess of sulphur dioxide is passed through a solution of nitrosulphonic acid $O_2N{\cdot}SO_3H$ in concentrated sulphuric acid, and to be the cause also of the purple colour of Gay-Lussac acid when sulphur dioxide is in excess in the exit gases from the chambers—

(3) 
$ON<^{OH}_{SO_3H}=NO+H_2SO_4$.

(4) $2NO+O+H_2O=2HNO_2$.

Divers (J. Soc. Chem. Ind. 1911, 10, 594) has again modified Raschig's theory. He believes that this transitory substance, identical with the compound which gives the colour to purple acid, has the composition $H_2N_2SO_6$, which he calls *nitroxysulphuric acid*, and that it is the only intermediate substance formed in the reaction.

His views are represented as follows—

(1) $2HNO_2+SO_2=H_2N_2SO_6$.
(2) $H_2N_2SO_6=2NO+H_2SO_4$.
(3) $2NO+O+H_2O=2HNO_2$.

Wentzki (Zeitsch. angew. Chem. 1910, 1707; 1911, 392) criticises Raschig's and Lunge and Berl's views, and is of opinion that neither nitrosylsulphuric acid (chamber crystals) nor the blue compound can exist in the chamber when excess of sulphur dioxide is present, and that sulphuric acid may be produced from sulphur dioxide, nitrous gases, and water without the formation of any intermediate compounds, as in Weber and Berzelius' early theory.

The blue compound he calls *nitrosylous sulphuric acid*, and he gives it the constitution


$HO{\cdot}SO_2{\cdot}\underset{\underset{O}{\vee}}{ON{\cdot}NO}{\cdot}SO_2{\cdot}OH$.

Jurisch (Chem. Zeit. 1910, 1065) and Manchot (Zeitsch. angew. Chem. 1910, 2113, and 1912, 1055) criticise Raschig's formulæ for the composition of chamber crystals and purple acid.

Reynolds and Taylor (J. Soc. Chem. Ind. 1912, 367) also unfavourably criticise Raschig's conclusions, and support the early simpler theory.

Whichever of these various views of the nature of the chemical reactions taking place be regarded as most probable, and it is impossible to enter here into the details of the experimental evidence in favour of each, no doubt whatever can be entertained that none of them accounts for the whole of the chamber phenomena; for even with the best-designed and most perfectly working system of nitre recovery, there is always a loss to be accounted for, which amounts to at least 2 parts of nitre per 100 parts sulphur burned as pyrites, the average loss being 3–4 parts.

Considerable difference of opinion exists as to what proportion of this is lost by incomplete absorption in the Gay-Lussac tower either as NO or N_2O_3 and N_2O_4; but this cannot account for the whole of the loss; there remains a very considerable proportion which can only be put down to other chemical reactions taking place in the chambers and causing reduction of the higher oxides of nitrogen to nitrous oxide, nitrogen, or other nitrogenous compounds, or even to ammonia.

The loss through incomplete absorption may be called mechanical loss. Figures have been obtained by Lunge, Davis, Jackson, Mactear, and others, indicating amounts of escape equivalent to from 1 to 1·75 parts of nitre per 100 of sulphur burnt as usual proportions; whilst Hurter, Eschellmann, and others consider 0·25–0·5 as more nearly the amount thus lost on the average with efficient plant in good working order. From the results obtained in a variety of works Hurter concluded (Chem. News, 39, 170) that the total loss of nitre from mechanical sources (*i.e.* defective absorption, formation of nitric oxide, leakages, and solution in chamber acid jointly) does not amount to as much as 25 p.c. of the nitre charged, at least 75 p.c. being lost by chemical secondary changes. E. K. Muspratt states (J. Soc. Chem. Ind. 1884, 137) that the result of experiments made in ten different works by a committee of the Alkali Makers Association was that the total loss by non-absorption in the Gay-Lussac tower averaged close to 20 p.c. of the nitre used, that being 4 parts per 100 of sulphur burnt. Eschellman found (*ibid.* 1884, 134) that out of 2·75 parts of nitre per 100 of sulphur burnt, 0·33 part (12 p.c.) was accounted for by non-absorption in the Gay-Lussac tower of soluble nitrogen oxides, and 0·19 part more (7 p.c.) by the formation of nitric oxide, representing a total of 0·52 part (19 p.c.) of loss due to available nitrogen oxides of all kinds; to which 0·08 part (3 p.c.) must be added for leakages and retention in the acid; thus leaving 2·15 parts (78 p.c.) not accounted for by mechanical losses, but destroyed by secondary chemical changes.

On the other hand, Lunge, Benker, Sorel, and others are of opinion that the greater proportion of the loss is due to incomplete absorption, owing to the fact that the coefficient of solubility of N_2O_3 in sulphuric acid is immensely reduced by its enormous dilution in the exit gases with oxygen and nitrogen, and that, therefore, its complete absorption is an impossibility. Sorel has attempted to prove in a special instance (Zeitsch. angew. Chem. 1889, 279) that the exit gases were bound to carry away N_2O_3 equivalent to 3·09 parts nitre per 100 sulphur burnt, and Lunge states (Sulphuric Acid and Alkali, vol. i. pt. ii. 954) that it is extremely difficult by ordinary analytical methods to estimate the quantities of N_2O_3 or N_2O_4 passing away into the exit gases, whilst the escaping NO is still more difficult to determine accurately.

Considerable support has been given to the view that the mechanical losses constitute the greater proportion of the total loss by some experiments made by Inglis at Silvertown (J. Soc. Chem. Ind. 1907, 668). He condensed a number of samples of the exit gases by means of liquid air, and afterwards separated the various constituents by fractionation. He was able to account for between 50 and 60 p.c. of the loss as due to incomplete absorption, partly as N_2O_3, and partly as NO, the total loss being 2·58 parts nitre per 100 parts of sulphur burnt. However, even his figures leave some 40 p.c. loss of nitre to be accounted for as chemical losses. At one time the Glover tower was blamed, it being supposed that considerable reduction of the nitrous gases to nitrous oxide by the excess of sulphur dioxide present took place there, but this has been practically disproved by the fact that quite as good results are obtained when nitric acid is run through the tower as when it is introduced into the chambers direct; whilst the quantity of available nitrogen oxides contained in the gases passing out of the tower can be shown analytically to correspond practically with the quantity contained in the nitrous vitriol run into the tower. It has also been suggested that there is some loss in the Gay-Lussac tower owing to the reducing action of arsenious oxide in the acid, or to the coke packing, but this is again disproved by the fact that with brimstone acid, where there is no arsenic present, the same loss occurs, and also with towers packed with other materials than coke.

Hence any material chemical loss must be confined to the chambers themselves in virtue of secondary reactions.

It has long been known from the experiments of Pelouze and Weber, more recently repeated and amplified by Lunge, that in contact with water or highly dilute sulphuric acid, higher oxides of nitrogen are slowly acted on by sulphur dioxide, with formation of nitrous oxide, thus—

$$N_2O_4+3SO_2+3H_2O=N_2O+3H_2SO_4$$
$$N_2O_3+2SO_2+2H_2O=N_2O+2H_2SO_4$$
$$2NO+SO_2+H_2O=N_2O+H_2SO_4$$

but in contact with stronger acid these actions take place either not at all or only extremely slowly. Consequently this action is only likely to take place where water or aqueous vapour is in excess, and that will be only in the immediate vicinity of the entering steam. That this reduction does take place is now generally admitted, but to what extent and what proportion of the loss is due to it there is considerable difference of opinion. Inglis, in the experiments alluded to above, could only account for about 10 p.c. of the loss as nitrous oxide in the exit gases, but Hempel and Heymann (Zeitsch. Elektrochem. 1906, 600) state that they obtained nitrous oxide in the exit gases from several works varying from 0·063 to 0·25 p.c. where 0·1 p.c. nitrous oxide would be equivalent to a loss of 4·3 parts nitre per 100 parts sulphur burnt.

A further reduction to nitrogen may also take place, but no proof of this is possible, whilst Raschig is of opinion that even ammonia may be formed by secondary reactions, but, in general, this would probably at once react with nitrous acid to give nitrogen and water. In some cases, however, where the chamber acid contains free sulphurous acid he has found traces of ammonia present in the acid (J. Soc. Chem. Ind. 1911, 172).

PURIFICATION.

All pyrites acid contains more or less iron, arsenic, and other substances derived from the ore employed, the contamination being considerably greater in the case of acid from the Glover tower than in that from the chambers. For many purposes these impurities are of no great importance, but for others, a purer acid is required, and various processes have been devised for removing these impurities, more especially from the chamber acid.

The chief impurities are arsenic, antimony, selenium, lead, iron, nitrous acid, and organic matter. The lead is almost entirely precipitated on diluting the acid; the iron largely separates during concentration, especially in the platinum still, organic substances being oxidised at the same time.

The most serious impurity is arsenic, which is nearly always accompanied by antimony and selenium, and nitrous acid.

Arsenic. Pyrites chamber acid made from Spanish pyrites usually contains from 0·05 to 0·2 p.c. arsenic, as arsenious oxide, whilst the Glover tower acid may contain as much as 1 p.c. or more, partly as As_4O_6 and partly as As_2O_5.

There are two methods employed on a considerable scale for the removal of arsenic. The first is by precipitation as arsenic sulphide by sulphuretted hydrogen. The latter is generated usually from ferrous sulphide by the action of weak sulphuric acid in wooden vessels lined with lead, and the gas passes into a tower packed with rows of horizontal wooden bars of triangular section covered with lead. A stream of chamber acid, from 100° to 110°Tw., is fed into the tower by a distributing arrangement at the top. Usually several generators are employed, so that, by charging them alternately a fairly uniform current of gas can be obtained, and the arsenic should be completely precipitated by the time the acid arrives at the bottom of the tower, from which it is run or blown into settlers. From these it runs on to sand filters, which it leaves practically free from arsenic; it should not contain more than 1 part in 500,000 parts acid. When alkali waste is available, the sulphuretted hydrogen is frequently obtained from that source. Nitrous acid, antimony, selenium, lead, &c., are removed also by this method, and except for the presence of a small quantity of iron the acid is practically as pure as brimstone acid.

The second method employed on a manufacturing scale for the removal of arsenic depends on the conversion of the arsenic into trichloride by treatment with hydrochloric acid, and the removal of the latter by heat. Common salt and barium chloride have been tried instead of hydrogen chloride, but they have not been successfully used on a practical scale. It is necessary that any arsenic oxide in the acid should first be reduced to arsenious oxide. The United Alkali Co. have patented a process for treating Glover tower acid with hydrogen chloride at 100°, and removing the liquid arsenic chloride which separates by blowing air through it; any arsenic oxide present is reduced by treatment with charcoal or sulphur (Eng. Pats. 7916, 16929, 16930, 1905; 23139, 1906).

The arsenic chloride may also be removed by treatment of the acid with certain mineral oils or oil from lignite tar (Hasenbach, U.S. Pat. 836034, 1906; and Vereiso, Chem. Fabrik. Mannheim. Fr. Pat. 368452, 1906).

Nitrous compounds or nitric acid are removed from sulphuric acid by heating with a small quantity of ammonium sulphate, whereby nitrite or nitrate ammonium is formed and at once decomposed with evolution of nitrogen or nitrous oxide. This is especially necessary where the acid is to be concentrated in platinum vessels in order to prevent serious corrosion of that metal.

Non-volatile impurities can only be completely removed by distillation of the concentrated acid. This is usually carried out in glass retorts, and is a troublesome operation owing to the liability of the retorts to crack: as the impurities accumulate in the retort they cause serious bumping. Scraps of platinum or quartz, &c., are frequently introduced to prevent this, or a slow current of air is passed through the boiling acid.

Iron is practically insoluble in 100 p.c. sulphuric acid, so that by bringing the acid up to that strength by mixing with fuming acid, and allowing to stand for some months, practically all the iron separates out.

CONCENTRATION.

Before the invention of the Glover tower chamber acid of 110°–120°Tw. was always evaporated down in leaden pans until the sp.gr. rose to about 140°–145°Tw., when the action on the lead became too great for further concentration to be thus possible. Such pans are still in use to a considerable extent; when contamination by fuel gases is immaterial they are heated by passing the flame over the liquid (top-firing); in which case the concentration may be carried to 150°Tw.; a certain amount of acid is always carried away in the current of fire gases when this method is employed. It escapes as a vesicular mist, which can only be condensed by filtration through fine granular material.

In other cases the pans are heated from below, the lead being protected from direct contact with the flame by iron plates. Waste heat from various sources is often used for heating the pans; sometimes they are mounted on the top of the kilns or on the burner gas flue, so as to partly utilise the heat of combustion of the sulphur burnt. Glover at one time employed a large platinum dish, placed inside the gas flue from his brimstone burner for concentrating chamber acid up to 140°Tw. High pressure steam passing through lead coils has also been used instead of directly fired pans.

For the further concentration up to from 93 to 98 p.c. H_2SO_4, glass or platinum stills were at one time chiefly used, but the great losses through breakages of the former and the great rise in the price of the latter, have led to their being displaced by other materials and methods of concentration, of which the Kessler and Gaillard processes have been most successful.

Glass stills, as first introduced by Chance Brothers at Oldbury, were worked separately, each being filled up with acid from the lead pans and heated until sufficiently concentrated, when the heat was withdrawn and the acid siphoned off into carboys through a platinum or lead siphon cooled by water. They were set in sand-baths and it was very important that they should be protected from cold draughts, especially towards the close of the operation, otherwise great losses were incurred through breakages. The continuous system of Gridley was a great improvement, a series of retorts being arranged at slightly different levels, each being connected with the next lower one by a siphon, so that when a slow stream of weak acid is run into the top one, entering at its highest part, the partly concentrated heavier acid passes through the siphon to the next, and so throughout the series, while concentrated O.V. is continuously discharged from the lowest. The acid vapours pass from each retort into a common pipe by which they are conveyed to a leaden coke tower and condensed by water. In the latest arrangement four retorts are enclosed in a glass case to protect them from draughts, and each is heated by a separate burner, coal gas being used as the heating agent, breakages being in this way reduced to a minimum. The acid is cooled by first passing through a platinum tube and then into a leaden vessel, both water-cooled. The strength of the acid obtained in these glasses does not usually exceed 93 p.c. H_2SO_4.

G. Veitch has patented (J. Soc. Chem. Ind. 1889, 983) the use of a series of flat-bottomed glass retorts arranged one above another on a stepped terrace within a common fire flue, the fire being placed at the lowest end, the flue narrowing upwards. The acid passes continuously through the whole series, leaving the lowest as concentrated acid.

Negrier (*ibid.* 1891, 46) patented a similar arrangement, using porcelain dishes instead of glass retorts, the lip of one dish projecting over the next below in the series. Two series of dishes are mounted side by side, fed from the same cistern, each dish resting on asbestos tissue and surrounded by sand up to the level of the upper rim; the supporting shelves are of iron.

Benker has improved the Negrier system by enclosing the porcelain dishes in a chamber of volvic lava. The flue gases are kept separate from the acid vapours, which are condensed in a lead-lined box filled with granular stoneware or silica. The dishes are covered with a thin layer of asbestos and silicate of soda cement, and the acid may be concentrated up to 97–98 p.c. H_2SO_4 (Zeitsch. angew. Chem. 1903, 1150). The porcelain dishes have, with advantage, been replaced latterly by vessels made of fused silica or metillure.

Webb uses a series of beakers arranged terracewise, the acid overflowing from one beaker and passing to the bottom of the next; they were at first made of glass, but later of porcelain. They can be worked without lead pans, 14–16 vessels in each series, but the fire gases and acid vapours are not separated, and a considerable amount of white fumes escape to the chimney (Eng. Pats. 2343, 17407, 18891, 1891). Other patents of Webb's showing modifications of the above are Eng. Pats. 1515, 1516, 1901; and D. R. P. 135886.

Levinstein (Eng. Pats. 19213, 1892; 2476, 2835, 1893) and Guttmann (Eng. Pat. 16220, 1898) have patented different arrangements of glass or porcelain beakers somewhat similar to Webb's.

Platinum stills have been considerably modified since their first introduction. Long, narrow, and shallow stills are now employed, sometimes with the bottom corrugated to increase the heating surface (Prentice system). In the Delplace system two shallow stills about 6 ft. long and 18 ins. wide are combined in series, the first receiving acid of about 144°Tw. from the lead pans; the vapours from each are condensed in a water-cooled platinum tube, the distillate from the second one being returned to the pans. The acid may be concentrated up to 98 p.c. in this way, and is cooled in a bottle-shaped platinum cooler, and afterwards in lead. Desmoutis puts concentric partitions in the stills, but any saving in fuel is counterbalanced by a greater loss of platinum. In the Faure and Kessler system platinum dishes are employed, provided with water-cooled leaden hoods; the condensed vapours run down the leaden covers to a lute. Platinum stills are appreciably attacked by concentrated sulphuric acid, the action being considerable when traces of nitrous acid are present. Platinum-iridium containing 10 p.c. iridium and upwards is much less readily affected than pure platinum. The loss of platinum by corrosion has been variously estimated at from 0·5–5·0 or even 10·0 grms. per ton of acid concentrated, according to the purity of the acid and the degree of concentration required. W. C. Heraeus (Chem. Zeit. Rep. 15, 36; also J. Soc. Chem. Ind. 1891, 460) found that platinum-iridium alloys containing respectively 0·01, 0·5, 5·0, and 10·0 p.c. iridium, are affected by hot sulphuric acid in the relative proportions 100, 90, 73, and 58 when sheets of these alloys are allowed to remain 40 days in a concentration apparatus, making 98 p.c. acid. With pure gold the relative proportion is only 13, or only one-seventh that of commercial platinum (0·5 p.c. iridium). Heraeus has, therefore, patented a process for covering the surface of platinum vessels with a compact adhesive layer of gold (Eng. Pat. 2499, 1891). Even when the price of gold was considerably higher than that of platinum the diminution of corrosion during use offered considerable pecuniary advantage, more particularly for 97–98 p.c. acid, and Heraeus stills have been adopted in several large German works (Lunge, J. Soc. Chem. Ind. 1892, 522). The acid to be concentrated must be very pure as crusts from impure acid damage the gold lining. Glover tower acid is seldom concentrated in platinum vessels owing to the hard crusts which separate.

Conroy (*ibid.* 1903, 465) has investigated the influence of various impurities in the acid, and the effect of temperature also on the corrosion of platinum vessels.

Cast-iron vessels have come into considerable use for the production of acid of high strength up to 98 p.c. H_2SO_4. Usually the acid is brought up to 93 or 94 p.c. in glass or platinum, and then to the highest strength in cast iron. There is a certain amount of action on the iron even at these strengths, but the contamination of the acid is not serious, as the sulphate mostly separates as an insoluble precipitate as the acid becomes fully concentrated. Sometimes cast-iron pans are employed with leaden covers, as in Faure and Kessler's system. If iron covers are used they must be kept hot so that no weak acid can condense on them. Cast-iron vessels seldom last more than 4–8 months. Weak acid can be concentrated in a deep cast-iron pan by running it on the surface of the heated acid, which is not allowed to drop below 90–93 p.c. H_2SO_4, the strong acid being at the same time withdrawn from the bottom. Cast-iron vessels are largely used for concentrating waste acids and impure Glover tower acid where the separation of impurities would render concentration in glass or platinum apparatus practically impossible. Hartmann (Chem. Zeit. 1899, 147) describes their use for concentrating waste acid from nitrating processes. Cast-iron dishes made of the so-called "neutral iron" by the A. G. für Bergbau und Eisen Luttenbetrieb at Kattowitz, Silesia, are now used by Hartmann and Benker for concentrating on the Benker system, and the acid comes out water white and not distinguishable from acid concentrated in platinum (Lunge's Sulphuric Acid, vol. i. 1176).

Dyson (Eng. Pats. 17699, 1893; 27769, 1896) employs a double row of stepped retorts made of iron and lined with a special acid-proof enamel for concentrating sulphuric acid from 100° to 168°Tw.

Zanner (Eng. Pat. 7999, 1901) places cast-iron pans lined with acid-proof stoneware slabs jointed with asbestos cement in the flue between the kilns and the Glover tower, and concentrates acid from 60°Bé. up to 66°Bé. by means of the hot gases. The pans are covered with earthenware slabs to keep the flue dust from falling into them and holes are provided for the escape of the distillate (Meyer, J. Soc. Chem. Ind. 1903, 781).

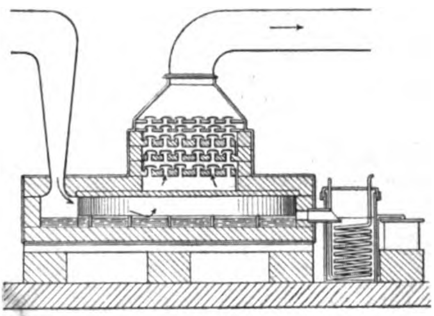


FIG. 12.

The Kessler process for the concentration of sulphuric acid by means of hot gases (Eng. Pats. 19215, 1891; 26169, 1898; 21376, 1900) has proved one of the most successful of the processes for this purpose. The hot gases from a producer charged with coke are drawn by means of a steam exhauster over the surface of the acid in a large shallow trough of volvic lava with a thick lead jacket, called the *saturex*, and then through a column, the *recuperator*, the lower section of which is of lava and the upper one of lead, where they come into intimate contact with a descending stream of weak acid which retains most of the acid vapours, but allows the steam to pass on to a large lead-lined condenser filled with coke crushed to the size of rice grains. This filters out the remainder of the acid vapour, and allows only aqueous vapour to escape. Fig. 12 gives a sectional elevation of the saturex and recuperator. The steam exhauster is placed in the connection between the recuperator and the condenser, and the steam and acid vapours pass downwards through the latter. A recent improvement has been made by replacing the steam exhauster by a compressed air jet; this has considerably reduced the amount of weak acid passing back from the condenser to be reconcentrated.

The concentrated acid is not so pure as that obtained in Benker's process, and seldom exceeds 95–96 p.c. H_2SO_4. A much larger condenser or filter is also required, owing to the dilution of the acid vapours with the fuel gases.

In the Gaillard process (Eng. Pat. 12538, 1906; Chem. Zeit. 1910, 173) the concentration is also brought about by means of hot gases. The dilute acid is sprayed by means of atomisers into the top of a cylindrical tower of volvic lava, in which it meets the hot products of combustion from a generator fed with coke. The hot gases enter near the bottom and leave at the top, from which they pass to a number of leaden boxes containing fine coke to remove the acid vapours. The acid arrives at the bottom of the tower in a concentrated state. This process has proved particularly useful for concentrating very impure chamber acid, and also for waste acids from petroleum refining. Stolzenwald (Zeitsch. angew. Chem. 1910, 175) and Duron (*ibid.* 1910, 2307) compare concentration up to 98 p.c. H_2SO_4 in Gaillard and Kessler plants with concentration in cast-iron boilers and pans.

Sulphuric acid of 100 p.c H_2SO_4 is usually obtained by adding fuming acid to ordinary oil of vitriol; this was formerly a very expensive process, and Lunge worked out a method for freezing out the acid from ordinary concentrated sulphuric acid by suitably cooling it, separating the crystals from the fluid portion and melting the former (Eng. Pats. 96, 1883; 4430, 1887). It was worked for a number of years in England at Widnes, and on the Continent at Petit-Quevilly and Griesheim, but it has been given up owing to the cheapening of fuming acid. It is described by Lunge (Sulphuric Acid, vol. i. 918) and by Osterberger and Capella (Bull. Ind. Soc. Rouen, 1889, 307).

PRACTICAL YIELD OF SULPHURIC ACID AND LOSSES DURING MANUFACTURE.

100 parts of sulphur charged into the kilns as brimstone or pyrites should theoretically yield 306·25 parts H_2SO_4. This yield is never obtained in practice, the chief sources of loss being—

(1) Sulphur is left in the ashes or cinders as sulphide, sulphate, &c. In the case of brimstone this is usually negligible, but with pyrites the sulphur left in the burnt ore may vary from 1 p.c. in the case of certain non-cupreous ores, practically free also from lead and zinc, to 2·5–3 p.c. in ordinary cupreous Spanish ores (Rio Tinto, Tharsis, Esperanza, &c.), and may reach 7 or 8 p.c. in the case of inferior ores containing much lead or zinc, or with good ores owing to faulty construction or working of the burners.

(2) Sulphur may sublime, when it will condense in the flues or in the acid itself and is lost.

(3) Loss occurs by leakages of gas during charging and working the kilns, potting nitre, and through cracks and holes in the chamber walls due to corrosion if they are not kept in good repair; and by leakages of liquid acid from chambers, siphons, tanks, &c.

(4) Sulphur escapes in the exit gases either through incomplete conversion of sulphur dioxide into sulphuric acid, or by incomplete condensation of the suspended vesicles of the latter substance.

Loss by incomplete conversion mainly depends in the first place whether Gay-Lussac towers are used or not; if they are used the sulphur dioxide escaping cannot amount to more than 2 p.c. of that equivalent to the sulphur burnt without causing a great loss of nitre through the formation of much nitric oxide, and it may be kept below 1 p.c. if the chamber space is ample (18–20 feet per lb. of sulphur burnt), the Gay-Lussac tower is well-proportioned and carefully packed, and the working of the whole process is under skilled supervision.

Under such conditions 100 parts of sulphur (as pyrites) charged into the kilns may be accounted for thus—

Left unburnt in 'cinders' . . .	5–6 parts.
Losses through leakages and incomplete conversion . . .	2–3 „
Total losses . . .	7–9 „

leaving 93–91 parts obtained as sulphuric acid, which is equivalent to 285–278 parts H_2SO_4 per 100 sulphur charged.

Even where only 11–12 cb. ft. chamber space per lb. sulphur burnt is employed, as good a yield may be obtained, provided that the capacity of the absorbing towers is considerably increased.

From brimstone 295–300 parts may be obtained per 100 sulphur charged, losses from incomplete burning being usually insignificant.

Where no Gay-Lussac tower is used the loss from incomplete conversion and condensation may be much greater, even when 25–30 cb. ft. chamber space per lb. sulphur is employed.

Consumption of nitre. As regards loss of nitre both with and without Gay-Lussac towers, the figures obtained in different factories vary very considerably; but, in general, the nitre used per 100 parts of sulphur burnt varies between 2·5 and 4 p.c.,[1] where Gay-Lussac towers are employed, and averages about 10 p.c. when they are absent. The more recent improvements of the chamber process have resulted in a great increase in the capacity of the chamber plant in many instances without any serious increase in nitre consumption.

Guttmann (J. Soc. Chem. Ind. 1903, 1332) states that Meyer, for his circular chamber system, guarantees a maximum consumption of 2·7 p.c. nitre, using 11·6 cb. ft. chamber space per lb. of sulphur burnt; with intermediate towers, fans and atomised water in place of steam, this may be reduced to 1·8 p.c. nitre.

Lüty (Zeitsch. angew. Chem. 1905, 1253), in describing Niedenführ's system, states that with 7–9 cb. ft. chamber space only 2·2–2·45 p.c. nitre is required.

The Alkali Works Report for 1906 gives particulars of a chamber system in which steam has been completely replaced by atomised water, whereby the chamber space has been

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[1] On the Continent the consumption of nitre is stated in a number of different ways. Usually the percentage is calculated on the acid made either in the form of chamber acid, acid of 1·7 sp.gr. or 100 p.c. H_2SO_4. Frequently it is stated in terms of nitric acid of 1·33 sp.gr., instead of sodium nitrate

reduced from 16·2–10·33 cb. ft. per lb. sulphur, and the nitre consumption from 4·23–2·87 p.c.

Littmann (Zeitsch. angew. Chem. 1906, 1177) claims that by allowing the gas from the Glover tower to enter the first chamber by six inlets at intervals along the top instead of by one at one end, he was able to reduce the chamber space from 14·5–12·9 cb. ft., and the nitre consumption from 3·6–2·9 p.c.

Falding (Eng. and Mining J. 1909, 441), in describing his system in which he combines one large chamber of considerable height compared with its length or breadth, with a cooling tower before the Gay-Lussac tower (U.S. Pat. 932771, 1909), states that with a chamber space of 7 cb. ft. per lb. of sulphur burnt, he only uses 2·8 p.c. nitre, and later (J. Ind. Eng. Chem. 1913, 223) he states that the chambers can be worked with only 1 to 1·5 per cent. nitre, using the same chamber space. On the other hand, Nemes (Zeitsch. angew. Chem. 1911, 387) adversely criticises the intensive system of working, and contends that the nitre consumption invariably rises with, and much more rapidly than, the yield per cubic metre; more supervision is required, and the cost of production of the acid is increased. He gives figures which differ considerably from the results quoted above.

Petersen (Zeitsch. angew. Chem. 1911, 877) replies to Nemes, giving the results obtained by Falding's and Meyer's systems in order to refute his statements.

Hasenclever (J. Soc. Chem. Ind. 1911, 1291), in the Hürter memorial lecture, gives it as his opinion that 11 cb. ft. per lb. of sulphur burnt is about the limit for chamber space without unduly increasing the cost of chamber repairs.

The nitre consumption in the Opl tower process as worked at Hurschau is given by Hartmann (Zeitsch. angew. Chem. 1911, 2302) as equal to 2·25 p.c. on the sulphur burnt, whilst the reaction space of the system is 0·53 cb. ft. per lb. 1·7 acid (approx. 2 cb. ft. per lb. sulphur).

Petersen (Zeitsch. angew. Chem. 1912, 762) compares the tower system with Falding's to the advantage of the latter.

MANUFACTURE OF FUMING ACID.

The various processes for the production of fuming acid, which have been at different times patented and put more or less in actual operation, may conveniently be grouped in two divisions—namely: (1) those depending on the action of heat on some metallic sulphate, whereby decomposition is brought about with evolution of sulphur trioxide, more or less further decomposed into sulphur dioxide and oxygen according to the temperature employed; (2) those in which the essential action is the surface or catalytic action of certain solids in bringing about union between sulphur dioxide and oxygen.

(1) Processes of Distillation of Sulphates.

The substance most largely employed, before the development of the contact process, as a source of fuming acid, was sulphate of iron, formerly in the form of 'copperas' or 'green vitriol' (ferrous sulphate), carefully dried so as to deprive it of most of its water of crystallisation and partially peroxidised during the process; latterly in the form of crude ferric sulphate prepared by long continued weathering of certain slaty minerals containing iron sulphide disseminated throughout them, lixiviation of the mass, evaporation of the mixed ferrous, ferric and aluminium sulphates dissolved out, and gently roasting so as to dehydrate the mass and completely peroxidise the iron present. The product thus obtained was heated in a series of clay retorts mounted together in a large 'galley' furnace, the sulphur trioxide was expelled and condensed in receivers previously charged either with a small quantity of water or preferably with oil of vitriol or weak fuming acid from a previous operation. Several successive charges were worked off into the same set of receivers, each retort holding not more than 3 kilos of 'vitriol-stone;' the residuum of impure ferric oxide, more or less brightly tinted, left in the retort constituted as important a product as the fuming acid itself, especially in the case of certain shades in the production of which so high a temperature was requisite that much of the anhydride was lost by splitting up into sulphur dioxide and oxygen; by the use of various subsidiary processes the residue was converted into pigments of different shades and considerable value. By redistilling at a gentle heat the fuming acid thus prepared, almost pure sulphur trioxide could be obtained or fuming acid of any strength required. This process was worked in Bohemia from about the year 1790 until 1900, when it was given up, as it could not compete with the 'catalytic' or 'contact' process. R. Schubert proposed to effect the distillation under greatly diminished pressure in order to reduce the loss from decomposition of SO_3, and passed the vapours evolved over heated platinised asbestos to bring about the reunion of any SO_2 and O formed. Sonstadt (1875) proposed magnesium sulphate for use in place of ferric sulphate, but the high temperature required to decompose it causes much loss by conversion into sulphur dioxide and oxygen. Sodium pyrosulphate obtained by carefully heating sodium hydrogen sulphate, was proposed by Prelier in 1847, and repatented by Wallace in 1876; the reactions here are

$$Na_2SO_4+H_2SO_4=2NaHSO_4$$
$$2NaHSO_4=H_2O+Na_2S_2O_7$$
$$Na_2S_2O_7=Na_2SO_4+SO_3$$

so that the process is a continuous one, the neutral sodium sulphate resulting from the distillation being converted into sodium hydrogen sulphate by treatment with sulphuric acid, and so on, over and over again. Wolters mixed magnesium sulphate with the pyrosulphate, stating that the sulphur trioxide was given off at a lower temperature than with pyrosulphate alone. None of these processes appears to have met with much commercial success, but a method due to Wolters is said by Lunge to have been actually at work in several factories; sodium pyrosulphate was treated with sulphuric acid, when sulphur trioxide was formed, together with sodium hydrogen sulphate, thus:

$$Na_2S_2O_7+H_2SO_4=2NaHSO_4+SO_3.$$

The residual sodium hydrogen sulphate was heated to 300°–320°C. in a retort furnished with an agitator and connected with an air-pump, and converted into pyrosulphate again.

Winkler suggested applying the continuous principle to the ferric sulphate distillation process by heating the residue with sulphuric acid so as to reproduce the sulphate of iron. Scheurer-Kestner found that by heating to a bright red heat a mixture of 2 parts calcium sulphate and 1 of ferric oxide, much sulphur trioxide was evolved, comparatively little being broken up into sulphur dioxide and oxygen, until the latter part of the heating; addition of a little calcium chloride or fluoride to the mixture considerably retarded the decomposition. Cummings (Eng. Pat. 7355, 1886) heated bricks made of gypsum and clay in a kiln, whereby silicate of lime and alumina were formed, suitable for hydraulic cement, while sulphur trioxide was evolved, more or less decomposed into sulphur dioxide and oxygen.

(2) Catalytic or Contact Process.

It has long been known that when a mixture of sulphur dioxide and oxygen is passed through a tube containing heated platinum, combination is induced, and sulphur trioxide formed; Peregrine Phillips, a vinegar maker, of Bristol, was the first to utilise the reaction in vitriol-making, and so to dispense with the use of nitre; in 1831 he patented a process of this kind (Eng. Pat. 6096, 1831), brimstone being burnt in excess of air, so that the gaseous mixture contained sufficient oxygen, and the gases were passed through heated tubes containing finely-divided platinum. The sulphuric acid formed was absorbed in a lead-lined tower filled with pebbles, down which water trickled. The process proved unable to compete with the chamber process at the time, and the demand for fuming acid had not yet arisen. Nevertheless, Phillips must be recognised as the real inventor of the contact process which has made such enormous progress during the last 30 years, having superseded all other processes for the manufacture of fuming acid, and is also largely employed for the production of high strength non-fuming acid in place of the lead chamber process.

Although several other attempts were made to utilise the catalytic action of platinum for this purpose no real progress was made until the year 1875, when two proposals were brought forward for manufacturing fuming acid by catalytic action. In that year Squire and Messel (Eng. Pat. 3278, Sept. 18, 1875) invented a process for the manufacture of sulphur trioxide and fuming acid, in which ordinary oil of vitriol was decomposed by heat into sulphur dioxide, oxygen, and steam, the latter was removed by condensation, as in Deville and Debray's process for the manufacture of oxygen from vitriol, except that the sulphur dioxide was not removed with the aqueous vapour, and the sulphur dioxide and oxygen were recombined by passing over heated platinised pumice (The Alkali Trade, C. J. Kingzett, p. 25). In 1875 also Winkler (Dingl. poly. J. Oct. 1875, 128) suggested a process based on much the same lines in which platinised asbestos (prepared by dipping asbestos successively into platinic chloride and sal-ammoniac solutions and igniting) was to be employed as the 'catalytic' agent. The principal difficulty in applying this process industrially was the rapid corrosive action exerted upon that part of the plant where the sulphuric acid was decomposed by heat. Squire and Messel's process was started at Silvertown in April, 1876, and was worked for a number of years until superseded by other processes mentioned later.

Fuming acid was made in Germany also by this or a similar method in 1877 by Clemm at Mannheim, and later by Jacob at Kreuznach, and in 1882 by Meister Lucius and Brüning at Höchst. In 1881 at the Thann Chemical Works in Alsace, a process introduced by Squire and worked out during 1879–1880 in conjunction with Chapman, Messel & Co. of Silvertown, was started for the manufacture of fuming acid from brimstone burner gases. The latter were treated with water under a pressure of 4 atmospheres. The sulphur dioxide was expelled by steam, mixed with air and passed over heated platinised asbestos. The sulphur trioxide formed was absorbed by concentrated sulphuric acid, and the exit gases containing some unoxidised sulphur dioxide were passed back into the process. Soon afterwards a similar plant was started at Silvertown.

In 1878 Winkler (D. R. P. 4566) patented the use of a variety of catalytic agents of high activity, more especially such substances as asbestos, slag wool, infusorial earth, &c., or even organic bodies like cellulose or cotton wool, impregnated with platinum black by soaking in platinum chloride solution and reducing with sodium formate. Messel (1878) patented the employment of sulphur dioxide and oxygen made by burning sulphur in excess of electrolytic oxygen prepared by a dynamo machine. A somewhat similar patent was taken out by Lunge in 1888, pure oxygen obtained by Brin's process being employed. Neale (Eng. Pat. 1103, 1876) heated anhydrous sulphates or bisulphates in earthenware retorts and passed the mixture of sulphur dioxide and oxygen thus obtained over heated platinised asbestos, spongy platinum, or the oxides of iron, chromium, or copper. In 1882 Rath took out a patent for the use of ordinary burner gases from sulphur or pyrites burnt in air, passed through purifiers for removing dust and aqueous vapour, and then through vertical iron tubes containing surface-acting materials at a temperature below a full and a red heat. And in 1887 Hänisch and Schröder (Eng. Pat. 9188) worked out a process in which 25 p.c. pure sulphur dioxide, obtained by treating burner gases with water in a coke tower and expelling the sulphur dioxide by heat, as in their process for the manufacture of liquid sulphur dioxide, with 75 p.c. air were passed over heated platinised asbestos while under a pressure of 2–3 atmospheres. According to Lunge, this process was at work for some years in several large factories until the development of the contract process dealing with ordinary pyrites gases made it unprofitable.

In 1898 patents were taken out almost simultaneously by the Badische Anilin und Sodafabrik, by Meister Lucius and Brüning of Höchst, and by the Mannheimer Verein Chemischer Fabriken, for the manufacture of sulphur trioxide from ordinary pyrites gases by the contact process. They have been followed from time to time by other patents, giving particulars of later developments of these processes.

The best-known of these is that of the Badische Anilin und Sodafabrik (Eng. Pats. 19547, 19548, 19549, 1898). These patents give a general description of the process, and more details have been furnished by Dr. Knietsch in a lecture before the German Chemical Society (Ber. 1901, 4069). The pyrites burner gases have first to be purified from all substances that can affect the activity of the platinum of the contact mass. Arsenic, phosphorus, and mercury are the most injurious and the most difficult to remove from the gases; other substances which may also do harm either by mechanically enveloping the platinum or by chemically affecting it, are iron, lead, copper, antimony, etc.

The gases are first treated with a jet of steam in the dust flue; this helps to oxidise any sulphur which has sublimed, by thoroughly mixing the gases, and at the same time it moistens them and prevents any condensation of concentrated sulphuric acid in the cast-iron cooling pipes, and therefore the possible formation of gaseous arsenical compounds, such as arsenuretted hydrogen, which cannot be eliminated when once formed, and which find their way into the contact mass, and in time seriously diminish its activity. The gases are then cooled to 100°C. by water in a tubular lead cooler, the steam again serving a useful purpose by preventing the formation of hard crusts in the cooler, and by diluting the condensing acid to such an extent that it has no serious action on the leaden tubes. The gases are next repeatedly washed with water or dilute sulphuric acid to free them from all traces of mist or dust, and are finally dried by means of concentrated sulphuric acid. Before passing to the contact apparatus they are examined optically, to see that they are free from dust and mist, by looking through a layer some yards in length illuminated at the further end, and chemically by allowing a stream of the gas to bubble through water for 24 hours, and then examining the liquid for arsenic by the Marsh test. The sulphuric acid mist must be completely removed, as it acts as a carrier for arsenic and other injurious substances.

The pure and dry gas, containing about 7 p.c. SO_2 is next forced by means of a mechanical mover through the contact apparatus (Fig. 13). This consists of a number of narrow vertical iron pipes containing the contact substance, in an outer casing also of iron. A portion of the gas enters this outer casing near the bottom, passes up between the contact tubes to a chamber at the top, where it meets and mixes with the remainder of the gas which enters the apparatus there. The temperature of this mixture is regulated by the relative proportions admitted at top and bottom, and should be high enough to start the reaction when it reaches the platinum contact material. The mixed gases pass down through the contact tubes, and the temperature rises quickly owing to the rapidity with which the combination of sulphur dioxide and oxygen takes place, but it is kept from rising too high by the stream of gas passing up between the tubes from below. When sulphur dioxide and oxygen combine to form sulphur trioxide, 32,200 calories are set free, and unless it is checked, the temperature rises so high that the reverse action sets in, the sulphur trioxide being decomposed again into sulphur dioxide and oxygen. A portion of the gas may also be admitted at different levels into the apparatus in order to get the best regulation of the temperatures. If necessary the gases are heated before entering the apparatus by their passage through the tubular heat-interchanger or regulator, through which a portion of the hot gases leaving the contact apparatus pass.

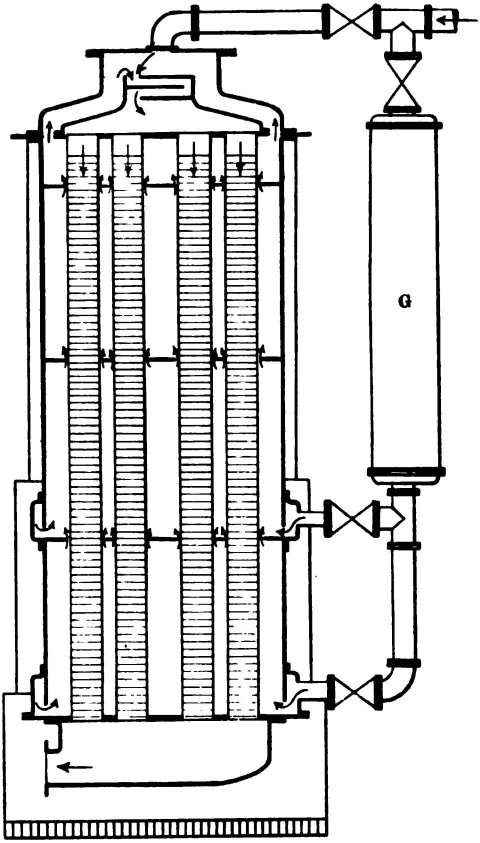

FIG. 13.—CONTACT APPARATUS.

The contact material consists of platinised asbestos containing about 10 p.c. platinum, and it is arranged in each vertical tube on perforated plates strung on a central rod, and separated from each other by short lengths of pipe in order that it should not get compressed and offer any considerable resistance to the passage of the gases.

The apparatus is first heated to above 300°C. in some convenient way, and the purified gases are then allowed to enter, the amounts, passing in at various levels, being regulated by the temperatures registered by thermometers at the top and bottom of the apparatus. The gases should reach the contact material at a temperature between 300° and 400°. The energetic action taking place at first causes a rapid rise to over 500°, followed by a gradual cooling, so that the gases leave the contact material at between 400° and 450°, at which temperatures a conversion of 96–98 p.c. may be obtained. The most suitable temperatures for maximum conversion will depend on a number of different factors, namely the quantity of gas passing through the apparatus, the percentage of sulphur dioxide and oxygen in the gases, the efficiency of the contact material, &c.

Other substances may be used instead of asbestos in combination with platinum as contact material. A mixture of salts consisting of a non-volatile base or salt of a non-volatile base which contains a radicle of a volatile acid, with a salt of a volatile base and non-volatile inorganic acid may be incorporated with platinum chloride and heated (Eng. Pat. 6828, 1901). Or oxides of iron, copper, or chromium may be used as foundations for the platinum (D. R. P. 140353, 1901). Two contact apparatus may be employed, 80–90 p.c. combination being obtained in the first, and the action completed in the second, the sulphur trioxide being removed from the gases before passing into the second apparatus. By this means the quantity of platinum employed may be considerably reduced (Eng. Pat. 12781, 1901).

The absorption of the sulphur trioxide takes place in iron vessels, wrought iron being used for making fuming acid, and cast iron for ordinary concentrated sulphuric acid (Eng. Pats. 1904, 1901, and 6829, 1901). Fuming acids containing more than 27 p.c. free sulphur trioxide have practically no action on wrought iron; by passing the gases through an absorber of this material, provided with a serrated hood dipping into acid of this strength or higher, and fed with dilute acid, fuming acid may be continuously obtained practically free from iron (containing less than 0·003 p.c.). To complete the absorption of the sulphur trioxide a similar absorber of cast iron is employed, also fed with dilute acid, but kept at a strength of between 97 and 98 p.c. H_2SO_4, at which strength almost perfect absorption may be obtained. If the attempt be made to absorb the sulphur trioxide with weaker acids or water, a considerable amount of white acid fume escapes from the apparatus, even although a number of absorbing vessels be employed.

Further details of the Badische process are given in U. S. Pats. 690062, 1901; 692018, 1902.

The processes worked out by Meister Lucius and Brünning and Höchst are described by Dr. Krauss and von Berneck in Lunge's Sulphuric Acid and Alkali, vol. i. 1374, and in various patent specifications. In their earlier process, the pyrites kiln gases were freed from impurities by washing with water, &c., dried by concentrated sulphuric acid and heated in a contact apparatus consisting of preliminary heating pipes and two contact retorts containing platinised asbestos. The gases left the contact apparatus at 400°–450°, and the sulphur trioxide was absorbed by concentrated sulphuric acid in cast-iron absorbers. After working in this way for some years, improvements were made by utilising the heat of the reaction for heating the incoming gases (Eng. Pat. 6057, 1898) and for regulating the temperature of the contact apparatus by the introduction of cold gases at various parts (Eng. Pat. 285, 1899). The greatly increased velocity of the reaction at high temperatures, up to a certain stage of the combination, next led to improvements for working the process, first at a high temperature, 530°, to obtain 75–80 p.c. conversion, and then at a lower temperature, 400°–450°, to complete it, either by working with two contact chambers kept at different temperatures, with cooling arrangements between, or by employing a long contact space, in which the gases enter at 530° and leave at about 430° (Eng. Pat. 1385, 1901). If two contact chambers are employed, a cheaper catalytist than platinum may be used in the first. The following list of active catalytic agents is given in this patent specification.

1. Platinum group metals.
2. Oxides and sulphates of Fe, Cr, Ni, Co, Mn, Ur, Cu.
3. Oxygen compounds of Al, Be, Zr, Ce, Di, La, Th, Ti, Si, and nearly all rare metals.
4. Mixtures of 1 with 2 and 3.
5. Mixtures of two or more substances of 2 and 3.

2, 3, and 5 can only be used at high temperatures, and hence may be used in the hot part of the contact apparatus.

The removal of the sulphur trioxide from the gases before passing into the second contact chamber and the more perfect utilisation of the heat of the reaction by means of heat interchangers in which the gases are cooled before the absorption of the sulphur trioxide and heated again for the completion of the reaction was the next improvement. Working in this way it is possible to use a cheaper catalytic than platinum in both contact chambers, which must be kept at the necessary high temperature, 80 per cent. conversion being obtained in the first, whilst 80 per cent. of the remaining 20 per cent. SO_2 is oxidised in the second, making 96 per cent. altogether; additional heat may also be obtained from the hot burner gas by passing the purified gas through a tubular economiser placed in the dust-chamber (Eng. Pat. 2368, 1901). Further particulars of the Hochst processes are given in Eng. Pats. 3161 and 4026, 1902; D. R. PP. 135887, and 169728, 1902.

In the process of The Mannheimer Verein Chemischer Fabriken (Eng. Pats. 17266, 1898; 1859, 3185, 24748, 1899; 18206, 1902; U. S. Pat. 690133, 1901) the air supplied to the pyrites furnaces is previously heated and dried, and the hot dry gases at about 700° pass at once into an iron-cased chamber containing ferric oxide (burnt ore) in pieces resting on a revolving grate. 60–65 p.c. of the sulphur dioxide is said to be here converted to sulphur trioxide, and at the same time the arsenic is retained by the oxide of iron. The latter is renewed from time to time as its catalytic activity diminishes. The gases pass on to an absorbing apparatus where the sulphur trioxide is removed, and are then forced by a fan-blast through filters of porous, granular, or fibrous substances to remove the last traces of impurities. They are now reheated before entering the final contact apparatus, which consists of a chamber containing removable iron frames supporting a net-work of platinised asbestos or other platinised fabric, in superposed compartments where the combination is completed.

The sulphur trioxide is then absorbed as before.

Copper oxide, chromium oxide, or manganese oxide or their sulphates may be used instead of ferric oxide as contact material for the hot gases (Eng. Pat. 4610, 1901).

Additional details of this process are given in a paper by Wilke (J. Soc. Chem. Ind. 1906, 4).

The chief features of the Schroeder-Grillos process (Eng. Pats. 25158, 1898; 17034, 1900; 10412, 1901) and its development are described in three papers read before the New York section of the Society of Chemical Industry (J. Soc. Chem. Ind. 1903, 348). The gases are purified by first cooling them to the ordinary temperature, passing them through scrubbers or washing towers fed with water or dilute acid, and finally through wet filters of large area containing a very fine coke packing or a fibrous material such as asbestos or cotton wool, and drying them by means of concentrated sulphuric acid. They are then preheated to 260°–280°, and passed into the bottom of a chamber set over a fireplace. In this chamber the contact mass is spread on perforated iron plates superposed one above the other, separated by partitions with central openings, by which means the gases are thoroughly mixed before passing from one layer to the next. The contact material is prepared by mixing solutions of a platinum salt with other soluble salts such as magnesium sulphate or a soluble phosphate, evaporating to dryness, and granulating. When heated in the contact apparatus the platinum separates and a very porous material is obtained, or platinum chloride may be mixed with a liquid or pasty material or a substance which melts in its own water of crystallisation, and the mixture dried in the contact apparatus by passing hot gases through it. The advantages claimed for this kind of contact material are that it is easily regenerated when its activity decreases by treating with water and regranulating, and that it offers little resistance to the passage of the gases. The heat is regulated so that the gases leave the contact apparatus at between 350° and 400°, and the sulphur trioxide is absorbed in a scrubbing tower after passing through suitable coolers.

At Freiberg (Lunge's Sulphuric acid, vol. i. 1409) the pyrites gases are purified exclusively by filtration (without any washing or drying apparatus) through a set of lead towers packed successively with coke, charcoal, wood shavings, and cotton wool. From the last tower the gases are aspirated by a fan-blast, and propelled into the contact apparatus, which consists of five horizontal retorts in a furnace heated by means of a gas producer. The contact material consists of platinised pumice or platinised unglazed porcelain containing 3–4 p.c. platinum. The temperature is kept between 440° and 460°, and the combination obtained varies between 45 and 90 p.c., depending on the percentage of sulphur dioxide in the gases. The sulphur trioxide is absorbed in towers fed with concentrated sulphuric acid and the uncombined gases are treated in vitrol chambers.

In Rabe's process Lunge's Sulphuric Acid, vol. i. 1415; Eng. Pat. 3327, 1901) the pyrites gases, after leaving the dust chamber, are sprayed with water in a porcelain-lined conduit, until the temperature is reduced to a point at which condensation of the fluid contents cannot yet take place, and then through a Glover tower fed with cold dilute sulphuric acid to cool them. They then pass through filter beds consisting of layers of granular coke of successively diminishing size, or through fibrous materials such as asbestos, the surface of which may be washed with water from time to time. The gases are thus obtained quite free from dust, and are further purified from non-neutral elements of a gaseous nature such as hydrogen chloride by means of bisulphites in granular form or in concentrated solution, and dried by concentrated sulphuric acid. The contact apparatus is a wide chamber containing platinised asbestos spread on sieves and the gases are heated up to the necessary temperature before entering it. The sulphur trioxide is absorbed in specially constructed reaction towers by concentrated sulphuric acid.

The Tentelen process as carried out at the Tentelen Chemical Works, St. Petersburg, is described in the British patents mentioned below. The burner gases after leaving the dust-chamber are cooled down to the ordinary temperature by passing down a circular tower built of lead surrounded by a water-jacket and cooled internally by means of a number of hollow vertical plates through which water continually flows (Eng. Pat. 14670, 1911). They next pass up through a filter of large area packed with coarse coke and then down through a similar filter containing very fine coke which removes all acid mist. The purification is completed by passing the gases through a series of washers containing an aqueous solution of an alkali or milk of lime or other alkaline earth to remove gaseous impurities as HCl, SiF_4, etc. (Eschellmann, Eng. Pat. 12213, 1907).

After drying, the pure gas passes through a heat interchanger or regulator to the contact apparatus. The first portion of the latter consists of a large empty vessel of considerable area, at the bottom of which is spread a layer of the contact material (platinised asbestos) on a perforated plate with projecting truncated pyramids which radiates its heat into the space above containing the incoming gases. By this means the temperature in the contact mass is not allowed to rise too high, and the conversion is completed in the lower narrower portion of the apparatus where the contact material is arranged in 25 thin layers on perforated plates and which is carefully protected against loss of heat (Eschellmann and Harmuth, Eng. Pats. 11969, 1902; 20952, 1904; 23419, 1909). After passing through the heat regulator again, and a small air cooler, the SO_3 is absorbed in a specially designed absorbing tower by concentrated sulphuric acid (Eschellmann and Harmuth, Eng. Pat. 22095, 1907).

A great many other patents have been taken out in recent years in connection with the contact process.

For purifying the burner gases Raynaud and Pierron (Eng. Pat. 16253, 1900) condense them in a porous material like kieselguhr, and after an interval expel them again by heat. The impurities are left behind. Eschellmann and Harmuth, U.S. Pats. 937147–937148, recommend the use of coke filters for removing lubricating oil from the purified gases before allowing them to enter the contact chamber.

Herreshoff (U.S. Pats. 940595, 950596, 955067, 969868, 1910) describes methods for cooling and purifying the burner gases by bringing them into intimate contact with weak acid in scrubbing towers and cooling pipes.

Messel (Eng. Pat. 22672, 1909) passes the burner gases over granulated coke or other carbonaceous material at a temperature above 300° in order to reduce any sulphur trioxide or sulphuric acid present to sulphur dioxide. In this way the acid mist which acts as a carrier for impurities is decomposed, and the whole of the sulphur dioxide and sulphur trioxide originally in the gases is obtained as sulphur trioxide and sulphuric acid in a pure condition.

Herreshoff (U. S. Pats. 719332 and 719333, 1903) employs two or more contact chambers with heat interchangers between. Ferguson (U. S. Pats. 723595, 723596, 1903) recommends the introduction of air into the gases in the interchangers to increase the content of oxygen, and (U. S. Pat. 857389, 1907) describes a long narrow contact apparatus furnished externally with ribs between which asbestos can be packed to regulate cooling by external air.

Raynaud and Pierron (Eng. Pat. 16254, 1900) suggest the use of different strengths of platinised asbestos in different parts of the contact apparatus in order to keep the temperature uniform. For absorption of sulphur trioxide, Herreshoff (U. S. Pats. 737233, 737626, 722981, 1903) describes apparatus suitable for this purpose.

Contact substances. The most important of these is platinised asbestos. It may be prepared of any strength up to 80 p.c. platinum by soaking asbestos in an alkaline solution of platinum chloride mixed with sufficient sodium formate to reduce the platinum, and heating to 70–80°. The platinum black is precipitated on the fibre, and the salts can be washed out with water without removing any of the platinum.

Another method of preparing it is by soaking the asbestos with a mixture of platinum chloride solution and methylated spirit, and setting fire to it.

Many other substances besides asbestos have been suggested as carriers for the platinum. Pumice, porcelain, oxides and sulphates of iron, copper, and chromium, soluble sulphates and phosphates have already been mentioned. Others are clay, glass, wool, kieselguhr, and sulphates of barium and calcium.

Revivification of inactive platinum contact masses. The Badische Anilin and Sodafabrik (D. R. P. 148196) treat the contact mass with dry sulphur dioxide or purified burner gas containing an excess of sulphur dioxide and little oxygen at the temperature of the contact process to remove arsenic and other impurities; or else with gases containing volatile compounds of chlorine.

D. R. P. 135887, 1902, recommends the admixture of steam with the purified gases for removing arsenic from the platinum contact material.

For catalytic bodies other than platinum, Eng. Pat. 1385, 1901, of Meister Lucius and Brüning already referred to, gives an extensive list.

THEORY OF THE CONTACT PROCESS.

The earlier workers of this process, Squire and Messel, Winkler, &c., were of opinion that a stoichiometrical mixture of sulphur dioxide and oxygen would give the best results, and endeavoured to work with these proportions, but never obtained anything like complete combination. In fact, complete conversion in one operation is theoretically impossible under these circumstances. This was first pointed out by Knietsch in the paper already referred to (Ber. 1901, 4093). From the results of a large number of experiments with mixtures of sulphur dioxide and oxygen, he showed that it is necessary to have an excess of one of the constituents present in order by mass action to eliminate the other completely, through its combining with the preponderating constituent to sulphur trioxide. The results of his experiments are illustrated by a series of curves (Figs. 14 and 15) showing the influence on the reaction of variations in temperature, composition of the gases, rate of flow for a definite amount of contact substance, and also of various contact substances. They show that it is necessary to have present an excess of oxygen, in order to obtain anything like complete combination of sulphur dioxide and oxygen to sulphur trioxide, and that if nitrogen is present it only acts as a diluent affecting the rate of combination, but not the percentage conversion.

Curves S, S′ and S″ show the course of the reaction using gases containing sulphur dioxide and oxygen in stoichiometrical proportions with which a quantitative conversion is not obtainable.

The formula of conversion should be written $2SO_2+nO_2=2SO_3+(n-1)O_2$, where n should not be less than 2.

Taking a technical burner gas containing 7 p.c. SO_2, 10 p.c. O, and 83 p.c. N, which is passed through a porcelain tube containing platinised asbestos heated to various temperatures, it is found that the first trace of sulphur trioxide appears at a little above 200°, and that the conversion is practically complete about 400°, and remains so up to 430°. Above this temperature the sulphur trioxide gradually dissociates more and more as the temperature rises, till it is all again reduced to sulphur dioxide and oxygen at 900°–1000° (curve 1, Fig. 14).

On increasing the rate of flow of the gas, or decreasing the amount of platinum employed, the maximum percentage conversion obtainable decreases, but at the same time the temperature of maximum conversion increases, but in all cases, there is the gradual reversion of the reaction which becomes complete at between 900° and 1000° as before (curves 2, 3, 4 and 5). Between 200° and 450° the reaction of formation preponderates, but above 450° the dissociation of sulphur trioxide comes very rapidly into play.

If the gases are passed through an empty porcelain tube some combination takes place, a maximum conversion of 30 p.c. being obtained at 600° (curve P), but if we start with almost completely converted gases and pass them through a heated empty tube, we find that decomposition only begins to take place as the temperature approaches 800°, and is not quite complete even at 1200°, thus showing that sulphur trioxide once formed, is very stable at high temperatures in the absence of an active contact substance (curve D). If the tube is filled with pieces of porcelain the decomposition begins earlier and increases more rapidly as the temperature rises (curve E), but not to the same extent as in the presence of platinum. Knietsch concludes from the results of his experiments that only those contact substances will be able to produce a quantitative reaction in one operation which exhibit their maximum of activity below 450°. All substances such as oxide of iron which develop their maximum power only beyond this temperature can never produce a quantitative conversion of sulphur dioxide into sulphur trioxide, no matter how long they remain in contact with the gases. Up to now there is only one catalytic substance which fulfils the beforementioned conditions, and that is platinum, and it cannot be replaced by any other metal of the Pt- group with even approximately equivalent results. On the other hand, above 450° the velocity of the reaction increases rapidly as the temperature rises, so that a large amount of sulphur dioxide may be converted to sulphur trioxide by a small amount of platinum when working at a high temperature, although the conversion may not be more than 90 p.c., and then the reaction may be completed at a lower temperature by using a larger amount of platinum. Fig. 15 represents this increase in velocity with temperature very clearly. Or a cheaper catalytic such as oxide of iron may be employed in the first stage of the operation.

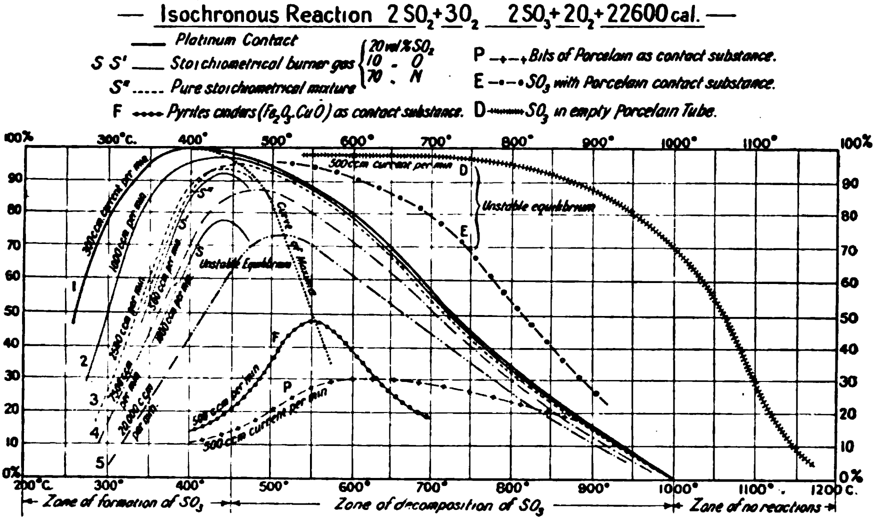

FIG. 14.

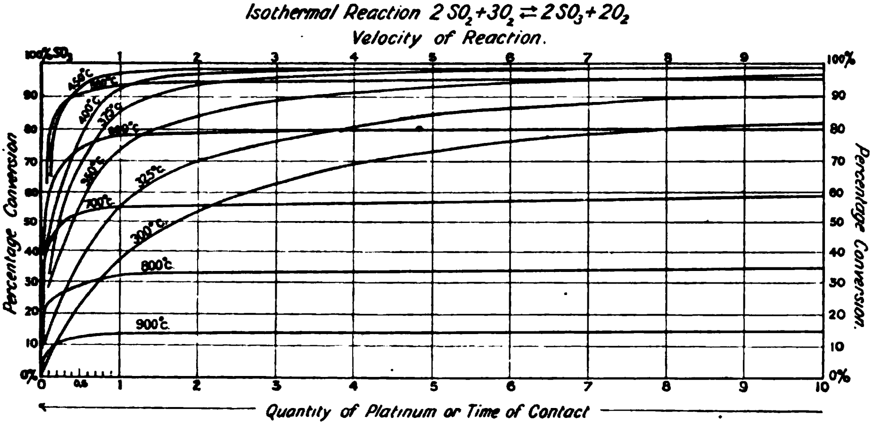

FIG. 15.

Brode (Zeitsch. angew. Chem. 1902, 1081) applies the laws of chemical equilibrium and velocity of reaction to the contact process and shows that to increase the reaction velocity and carry the reaction further towards completion, increase of sulphur dioxide and oxygen concentration and decrease of sulphur trioxide concentration are necessary.

The formula $K = \frac{C^2_{SO_3}}{C^2_{SO_2} \times C_{O_2}}$ shows that the ratio of sulphur trioxide to sulphur dioxide increases as the square root of the oxygen concentration. Also as the formation of sulphur trioxide lessens the volume, it must be favoured by increase of pressure.

Bodländer and Köppen (Zeitsch. Elektrochem. 1903, 559) state that in the reversible reaction $2SO_2+O_2 \rightleftharpoons 2SO_3$ equilibrium is represented by $\frac{(SO_2)^2\cdot(O_2)}{(SO_3)^2}=K$, and depends only on the relative concentrations of the reacting bodies, but the velocity depends on the absolute concentrations. Thus dilution with extra air retards the reaction at first, while it is rapid, but greatly accelerates it in the later stages.

By heating gaseous mixtures in a tube with platinum gauze, and measuring the diminution of pressure at constant volume, these chemists find that at temperatures between 182° and 341° the values of K approximate more nearly to $[(SO_2)^2\cdot(O_2)]$ than $[(SO_2)\cdot(O_2)]$ and that the velocity increases about 1·4 fold for each 10° rise in temperature. Also the concentration of the sulphur trioxide formed retards the reaction even at these low temperatures.

They also have determined the temperatures at which, with different gaseous mixtures of sulphur dioxide, oxygen, and nitrogen, definite percentages of the total possible amount of sulphur trioxide will be formed, when equilibrium is established. Above 650° the platinum absorbs oxygen.

Comp. of orig. mixture		Yield of SO_3						
SO_2	O_2	98 p.c.	96 p.c.	94 p.c.	92 p.c.	90 p.c.	80 p.c.	60 p.c.
At atmospheric pressure		°C.	°C.	°C.	°C.	°C.	°C.	°C.
66·6	33·3	425	476	497	520	538	597	668
11·69	5·85	378	423	452	473	489	543	553
10·0	8·04	450	483	503	518	531	576	635
8·0	10·62	467	505	518	537	548	592	648
7·0	10·0	467	504	518	535	547	590	647
6·0	13·23	477	513	530	545	557	602	658
4·0	15·81	483	521	539	554	565	611	666
2·0	18·45	488	527	543	558	570	615	671
At 10 atmospheres pressure								
11·69	5·85	428	477	504	527	543	605	680
10·0	8·04	503	538	558	576	589	639	703

Lucas (Zeitsch. Elektrochem. 1905, 457) repeated Bodländer and Köppen's experiments, and practically confirmed their results.

Bodenstein and Pohl (*ibid.* 1905, 373) adopted Knietsch's method of passing a stream of sulphur dioxide and air or oxygen over platinum in a quartz tube heated by an electric furnace, and determining the composition of the mixture before and after contact. They have also calculated from their results and tabulated the yields (percentage of SO_2 converted to SO_3) for different mixtures at different temperatures.

Bodenstein and Fink (Zeitsch. physikal. Chem. 1907, 1) describe further experiments dealing with the kinetics of the contact sulphuric acid process.

A large number of papers have also been published dealing more particularly with the ferric oxide contact process.

Keppeler (Zeitsch. angew. Chem. 1902, 809); Lunge and Pollit, J. Soc. Chem. Ind. 1902, 79; Lunge and Reinhardt (Zeitsch. angew. Chem. 1904, 1041; Kuster, *ibid.* 1904, 1512; Keppeler, *ibid.* 1908, 532, 577).

STATISTICS OF THE PRODUCTION OF SULPHURIC ACID.

The Chemische Industrie of Feb. 1, 1912, attempts to estimate the quantity of sulphuric acid produced in the chief countries of the world from the consumption of pyrites. Taking the years 1900–1910 it will be seen that in the four most important industrial countries England, France, Germany, and the United States, the consumption of pyrites in the last two countries during that period has steadily increased, while in England it has been practically stationary.

PYRITES CONSUMPTION IN 1000 TONS.

	England	France	Germany	United States	
1900	. 753	397	627	536	
1901	. 693	461	646	640	including brimstone.
1902	. 620	423	647	645	
1903	. 745	408	690	660	
1904	. 753	426	678	620	
1905	. 710	518	737	768	
1906	. 770	589	776	858	
1907	. 779	614	938	903	
1908	. 777	592	878	890	
1909	. 799	508	890	902	
1910	. 801	—	1008	1007	

Assuming a yield of 134 parts H_2SO_4 from 100 parts pyrites the sulphuric acid produced in 1910 would amount in tons to—

England	Germany	United States
1,073,000	1,350,000	1,349,000

To these figures must be added the amount of acid produced from brimstone, spent oxide, sulphuretted hydrogen, zinc blende, &c.

According to the 25th Alkali Report the quantity of brimstone burnt in England in 1883 was 17,295 tons equal to about 50,000 tons H_2SO_4, and it will, no doubt, be less now. For spent oxide no figures are at present available.

In 1910 the consumption of zinc blende in Germany was 430,000 tons, from which the greater part of the sulphur was utilised for sulphuric acid manufacture.

In France the production of sulphuric acid averaged about 900,000 tons during the last few years, and in Italy about 400,000 tons per annum.

In Russia in 1910 the production was 200,000 tons.

According to Wedge (Proc. 8th Int. Cong. Appl. Chem. 1912, 271, and J. Soc. Chem. Ind. 1912, 874) the production of sulphuric acid in the United States in the year 1911 amounted to 3,250,000 tons 50°Bé.=approx. 2,031,200 tons H_2SO_4.

Of this 2,665,000 tons were obtained from pyrites.
27,500 „ from copper sulphide ores.
285,000 „ „ zinc blende.
and only 25,000 „ „ brimstone. E. C. T.

SUMACH. True sumach consists of the dried and usually powdered leaves of the genus *Rhus* (order *Terebinthaceæ*), and is useful for tanning the finer kinds of leather, and also in dyeing and calico-printing on account of the tannin matter present in it.

Sicilian sumach, the variety most esteemed in this country and throughout Europe, consists of the leaves of the *Rhus Coriaria* (Linn.), a shrubby bush cultivated to a large extent in Sicily, where the sumach industry is of considerable importance. When the plant is about to flower the younger twigs are removed, dried in the sun, and subsequently beaten to remove the leaves and flower panicles. The sumach is imported sometimes in leaves, but more often in the form of powder, and should contain about 25 p.c. of tannin, although as much as from 27 to 32 p.c. may occasionally be found.

According to Löwe (Zeitsch. anal. Chem. 12, 128), the tannin matter present $C_{14}H_{10}O_9$, is ordinary gallotannin; indeed it is well known that when an aqueous extract of the sumach is boiled with dilute sulphuric acid, considerable quantities of gallic acid are produced. On the other hand, Strauss and Geschwender (Zeitsch. angew. Chem. 1906, 1121) who isolated the tannin according to Löwe's instructions, detected the presence of a methoxyl group, and suggest the formula $C_{32}H_{29}O_{11}\cdot OMe$.

Sicilian sumach contains also a trace of an ellagitannin and myricetin, $C_{15}H_{10}O_8$, to the extent of about 0·1173 p.c. (Perkin and Allen, Chem. Soc. Trans. 1896, 69, 1299), the latter colouring matter having been previously mistaken by Löwe (Zeitsch. anal. Chem. 1874, 12, 127) for quercetin.

Considerable quantities of sand and sometimes particles of magnetic iron ore, which cause black stains, are often to be found in sumach (Procter, Principles of Leather Manufacture, 1903, 271; compare also Trotman, J. Soc. Chem. Ind. 1904); and it is frequently highly adulterated in the ground condition with the leaves and twigs of various plants. Of these, the *Pistacia Lentiscus* (Linn.) ('schinia' or 'skeñs'), *Coriaria myrtifolia* (Linn.) (French sumach or 'stinco'), *Tamarix africana* (Poir.) (brusca), *Tamarix gallica* (Linn.), *Ailanthus glandulosa* (Desf.), *Ficus Carica* (Linn.), *Vitis vinifera* (Linn.), other species of the Rhus family, and also the ground branches ('gambuzza,' 'gammuzza') of the *R. coriaria* itself are known to be employed. These sumach adulterants also contain tannin matters, but for tanning and dyeing purposes are as a rule much inferior to sumach itself.

The *Pistacia Lentiscus* (Linn.) (mastic tree), a small tree about 20 ft. high with evergreen leaves, grows abundantly in Cyprus. The leaves of this plant constitute the most important sumach adulterant, and about 10,000 tons are said to be exported from Tunis to Sicily annually and re-exported thence (as sumach ?). According to Procter (*l.c.*) the leaves contain 12–19 p.c. of a catechol tannin. A good plump leather can be obtained from this material, but of a faintly reddish tint, the result being intermediate in character between those which are given by oak bark and sumach. Its presence in sumach is to be deprecated, and in many cases leads to injurious results. A considerable quantity, however, is consumed at Lyons in France as an assistant dyeing material for silk stuffs.

According to Perkin and Wood (Chem. Soc. Trans. 1898, 73, 374), these leaves contain a tannin closely allied to, if not identical with, ordinary gallotannic acid, as when an aqueous extract is boiled with dilute sulphuric acid a considerable quantity of gallic acid is produced. A second tannin or tannin glucoside is also present which, although possessing the general characteristics of the so-called 'catechol' tannins in that it yields a red phlobophane, and as noted by Procter, a reddish coloured leather, gives, by fusion with alkali, *gallic acid* and *phloroglucinol*.

In addition to these tannins, myricetin (probably as glucoside) $C_{15}H_{10}O_8$ is also present to the extent of about 0·15 p.c.

Tamarix africana (Poir.) is a small shrub or tree characterised by its twiggy branches and minute scale-like leaves. The small twigs are collected in Tunis and imported into Sicily for the adulteration of sumach (Procter).

According to Perkin and Wood (*l.c.*), the leaves contain a tannin probably identical with gallotannin, in addition to a small quantity of an ellagitannin. A trace of yellow colouring matter is also present and consists of a *quercetinmethylether* $C_{16}H_{12}O_7$.

The *Tamarix gallica* (Linn.) closely resembles in appearance the *T. africana* and flourishes in Cyprus, where the latter is not found. According to Procter, it contains 8·4 p.c. of tannin matter.

Ailanthus glandulosa (Desf.) is a tree of large size and handsome appearance, native of India and China but common on the Continent. The leaves contain 11·2 p.c. of tannin matter (Procter) and this resembles gallotannin, although a trace of an ellagitannin is also present (Perkin and Wood). Curiously enough, although so high a percentage of tannin is present, leather is scarcely tanned by an extract of these leaves, but is merely stained a dull dirty colour. This material is therefore of little use for tanning purposes, and as an adulterant of sumach exerts a deleterious influence. A small quantity of quercetin can be isolated from the leaves.

The leaves of the *Ficus carica* (Linn.) (common fig tree) contain 1·6 p.c. of tannin (Procter) and a trace of a yellow colouring matter (Perkin and Wood). Skin is untanned by an extract of these leaves, but acquires, during the process, a dirty olive tint.

Gambuzza consists of the small stalks branching from the main root of the *R. Coriaria* (Linn.) which are ground to powder and mixed with sumach. The material contains some quantity of a tannin resembling gallotannin, together with a trace of myricetin.

Attempts to detect the presence of these adulterants in sumach by chemical methods have not given satisfactory results, but should a prolonged boiling of the extract with dilute sulphuric acid cause the gradual precipitation of phlobophane, the presence of the leaves of the *Pistacia lentiscus* may be suspected.

More satisfactory results can be obtained by microscopical examination, and an elaborate work on this subject has been carried out by Andreasch (Sicilianischer Sumach und seiner Verfalschung, Wien, 1898); the book, however, is unsuitable for abstraction. A useful method, now generally adopted by leather trades chemists, has been devised by Lamb and Harrison (J. Soc. Dyers, 1899, 14, 60), and is based upon the behaviour of the leaf mixture with warm nitric acid. Under such treatment, the more delicate leaf structure of sumach itself is completely destroyed, whereas the strong cuticles of *Pistachia lentiscus, Coriaria myrtifolia, Tamarix africana* and *Ailanthus glandulosa* are unaffected and can then be readily recognised (compare also Lamb, *ibid.* 1904, 20, 265). Again, the leaves of the *R. coriaria* are very easily distinguished from those of other plants employed for their adulteration in that both upper and lower cuticles are covered with a dense growth of hairs (Priestman, J. Soc. Chem. Ind. 1905, 24, 231).

Venetian sumach or *Turkish sumach* consists of the leaves of the *Rhus Cotinus* (Linn.), a small tree the wood of which constitutes the yellow dyestuff known as 'Young Fustic.' The material contains about 17 p.c. of tannin, which resembles ordinary gallotannin, together with a trace of an ellagitannin. The presence of myricetin $C_{15}H_4O_2(OH)_6$ in these leaves is interesting, in view of the fact that in the wood itself, fisetin $C_{15}H_6O_2(OH)_4$ is present (Perkin, Chem. Soc. Trans. 1898, 73, 1016).

American sumach. The leaves of numerous varieties of *Rhus* are employed in the United States for tanning and dyeing purposes, and of these the *R. glabra* (Linn.) very largely takes the place of Sicilian sumach. It contains about 25 p.c. of a tannin closely resembling gallotannin, but produces a leather of very much darker colour than the Sicilian product.

Of the other varieties, *R. typhina* (Linn.) or 'Virginian sumach' (10–18 p.c.), *R. cotinoides* (Nutt.) (21 p.c.), *R. semialata* (Murr.) (5 p.c.), *R. aromatica* (Ait.) (13 p.c.) (Procter), *R. Metopium* (Linn.) (about 8·2 p.c. of tannin, probably gallotannin, together with traces of both quercetin and myricetin) (Perkin, Chem. Soc. Trans. 1900, 77, 427), *R. copallina* (Linn.), *R. pumila* (Michx.), and *R. Toxicodendron* (Linn.) are to be found in the States. Among these, *R. glabra* and *R. copallina* are considered to be worthy of extended cultivation.

In India, numerous species of the genus *Rhus* are known to exist (Watt's Dictionary, Economic Products of India), and again in Algeria the *R. pentaphylla* (Desf.) is used by the Arabs for tanning goat skins. Finally, the *Anaphrenium argenteum* (E. Mey.) (*R. Thunbergii*) (Cape of Good Hope), 28 p.c. of tannin (bark), probably of the catechol class (Procter), and the *Rhodosphaera rhodanthema* (Engl.) (*Rhus rhodanthema*) (New South Wales), 9·5 p.c. of tannin (leaves), resembling gallotannin, are worthy of mention. The latter plant, also known as the 'yellow cedar,' closely resembles the *R. cotinus*, and it is interesting to note that although the wood of this tree contains fisetin $C_{15}H_4O_2(OH)_4$, the colouring matter of the leaves is quercetin $C_{15}H_3O_2(OH)_5$ (Perkin, Chem. Soc. Trans. 1898, 73, 1017).

French sumach is derived from the *Coriaria myrtifolia* (Linn.), a low deciduous shrub, native of Southern Europe, and has been referred to above as an adulterant of Silician sumach. In addition to tannin (15·6 p.c., Procter), which consists probably of ordinary gallotannin together with a little ellagitannin, it contains the poisonous glucoside *coriamyrtin* (Riban, Chem. Zeit. 1867, 663) and a trace of quercetin (Perkin, Chem. Soc. Trans. 1900, 77, 428). According to Procter, the colour of leather tanned by these leaves is very satisfactory and practically equal to that produced by genuine sumach (*R. coriaria*). It is also employed in black dyeing.

Cape sumach consists of the leaves of the *Colpoon compressum* (Berg.) (*Osyris compressa, Fusanus compressus, Thesium colpoon*), and is much used in South Africa under the name of 'Pruimbast.' The bush is found in the mountains, where it grows to the height of about 6 ft., and only the younger leaves are gathered. These leaves contain about 23 p.c. of tannin (Procter) which has been isolated as a hygroscopic transparent glassy mass and is probably a catechol tannin glucoside. With boiling dilute acid, a reddish-brown phlobophane is gradually separated, and on fusion with alkali protocatechuic acid is produced (Perkin, Chem. Soc. Trans. 1897, 71, 1135). In addition to tannin there is also present a considerable quantity of the quercetin glucoside *Rutin* (Osyritrin) (Chem. Soc. Trans. 1910, 98, 1776). According to Procter, this material forms a useful substitute for Sicilian sumach.

In lieu of the *Colpoon compressum*, a tanning agent known as 'broach leaves' (botanical origin lacking) appears to be considerably employed in South Africa. It contains about 19·9 p.c. of tannin of the so-called 'catechol' variety, together with traces of both quercetin and myricetin (Chem. Soc. Trans. 1898, 73, 384).

Russian sumach consists of the leaves of the *Arctostaphylos Uva-ursi* (Spreng.) (Bearberry), and is said to contain about 14 p.c. of tannin, which, according to Perkin (Chem. Soc. Trans. 1900, 77, 424), consists of a gallotannin together with traces of an ellagitannin. Minute amounts of both quercetin and myricetin have been isolated from this material.

Considerable quantities of 'sumach extract' are now manufactured for dyeing and tanning purposes from genuine Sicilian sumach, and this is usually found on the market as a brown treacly liquid of about 52Tw. So-called *decolourised* extracts are also prepared to compete with ordinary tannic acid, and for this purpose the addition of blood albumen to the dilute extract at about 48°, then raising the temperature to 70°, and subsequently filter-pressing, gives the most satisfactory results. Sulphurous acid again is employed to brighten the colour of extracts and acts partly as a weak acid in decomposing the inorganic salts of the tannin or colouring matter and partly as a reducing agent. In this case it is usual to pass sulphur dioxide through the liquor before concentration (Procter). A. G. P.

SUNFLOWER, *Helianthus annuus* (Linn.). A Mexican plant, now grown in many warm countries for the oil contained in its seeds. The seeds, which differ greatly in size, according to the variety (3000 to 6000 seeds weighing 1 lb.), consist of a hard woody envelope and an oily kernel.

Average composition of the seeds (König):—

	Water	Protein	Fat	N-free extract	Fibre	Ash
Whole seed	8·6	13·7	31·3	18·0	25·4	3·0
Kernels .	6·7	26·3	44·3	16·4	2·8	3·5

According to Wiley (Bull. 60, 1901, U.S. Dept. of Agric., Div. of Chem.), the following represents the average composition of the products of American grown sunflowers:—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Seeds .	4·4	15·0	27·1	20·9	29·2	3·4
Seed shells	6·2	3·0	1·7	23·2	63·8	2·2
Kernels .	4·9	26·9	45·2	16·1	2·7	4·3

Hungarian grown sunflowers apparently yield more oil; Windisch (Landw. Versuchs-Stat. 1902, 57, 305) found the following:—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Whole seeds	6·9	15·2	28·9	17·4	28·5	3·2
Husks .	10·1	6·9	7·9	20·8	51·6	2·7
Kernels .	4·0	24·9	50·4	12·8	3·1	4·0

The principal proteid occurring in the seed is edestin (Osborne and Campbell, J. Amer. Chem. Soc. 1896, 18, 609; 1897, 19, 487) associated with heliantho-tannic acid. The edestin from sunflower seeds contains: C, 51·54 p.c.; H, 6·99 p.c.; N, 18·58 p.c.; S, 1·00 p.c.; O, 21·71 p.c.

Sunflowers are largely grown in Russia, the seeds being used to some extent as human food in cold weather, as food for poultry and cattle, but chiefly as a source of oil (*v.* OILS, FIXED, AND FATS). The leaves are sometimes used as food for farm animals, being often dried, powdered and mixed with meal for cattle. The stalks are used as manure, being rich in potash and lime, or sometimes, as fuel.

The plant requires much sunshine and prefers rich, dark soil. Excessive nitrogenous manuring is to be avoided, or the growth of stems and leaves is favoured at the expense of the seeds. About a ton of seeds per acre is the average yield in Europe.

The cake left after the expression of the oil from the seeds forms a valuable food for cattle. Kellner gives as its average composition—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
9·2	39·4	12·6	20·7	11·8	6·3

32·4 of the total 39·4 is digestible protein.

If the seeds are not husked or decorticated before the oil is expressed, the resulting cake is richer in crude fibre (up to 30 p.c.) and correspondingly poorer in albuminoids and fat.

The ash of sunflower seeds and of other parts of the plant was examined by American investigators (Wiley, Bull. 60, 1901, U.S. Dept. of Agric.; Div. of Chem.), who found it to contain—

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Whole seeds .	29·0	1·1	9·4	17·9	0·5	38·4	2·9	0·4	0·5
Stems . .	38·9	3·8	24·1	19·9	1·2	1·5	3·5	1·3	7·3
Leaves . .	8·0	0·9	44·0	21·5	2·8	3·3	4·5	13·8	1·5
Kernels of seed	25·5	0·8	6·6	14·7	0·4	50·8	1·0	0·2	0·0
Shells of seed .	47·4	1·0	20·9	15·9	1·1	6·8	5·0	0·8	1·5
Husks of seed .	55·7	1·7	20·1	9·5	0·9	3·7	2·9	2·0	4·6

Sunflowers are therefore an exhausting crop, making great demands on the nitrogen, potash, and phosphoric acid of the soil. H. I.

SUNSTONE *v.* FELSPAR.

SUPRARENINE *v.* ADRENALINE.

SUPERPHOSPHATES *v.* FERTILISERS.

SYENITE *v.* GRANITE.

SYLVANITE. A native telluride of gold and silver, $AuAgTe_4$ (Au, 24·2 p.c.; Ag, 13·3 p.c.; Te, 62·5 p.c.), of importance at certain localities as an ore of gold. It has long been known from Transylvania (hence the name 'sylvanite'), where it occurs on joint surfaces in porphyry as slender rod-like crystals aggregated, by twinning, into branching forms suggesting a resemblance to written characters (hence the old names 'graphic gold' and 'graphic tellurium,' Ger. *Schrifterz*). The crystals are monoclinic and possess a perfect cleavage in one direction, parallel to the plane of symmetry: this cleavage is of assistance in recognising the mineral. The colour is silver-white with a brilliant metallic lustre, but on exposure to light the crystals become dull; sp.gr. 8·2. It is found at Offenbánya and Nagyág in Transylvania, and at several places in Boulder Co. in Colorado, and Calaveras Co. in California. At Kalgoorlie in Western Australia it is found as large cleavable masses (L. J. Spencer, Min. Mag. 1903, 13, 271). L. J. S.

SYLVITE or *Sylvine*. Native potassium chloride (KCl). It crystallises as cubes or cubo-octahedra with perfect cubic cleavage, but, as proved by etching experiments, these possess a lower degree of symmetry (plagiohedral-cubic) than crystals of rock-salt (halite). The crystals are colourless or sometimes bright blue, and they are indistinguishable in appearance from crystals of rock-salt. The two minerals may, however, be readily distinguished by the colour they impart to the Bunsen-flame, by their sp.gr. (1·99 for sylvite, 2·15 for rock-salt), and refractive index (1·491 and 1·547 respectively for sodium-light). Good crystals are found amongst the abraum-salts at Stassfurt in Prussia and at Kalusz in Poland. As a granular incrustation intermingled with sodium chloride and other salts it has long been known on Vesuvian lava, and small cubes were found after the 1906 eruption. The latter are intimately associated with cubes of rock-salt, but without forming mixed crystals. L. J. S.

SYMPHOROL *v.* SYNTHETIC DRUGS.

SYNGENITE *v.* CALCIUM.

SYNTHETIC DRUGS or **MEDICINAL PRODUCTS.** The employment of synthetic coal-tar products in internal medication may be said to date from the introduction of 'kairin,' a synthetic substitute for quinine, discovered by O. Fischer in 1882. The unsatisfactory results attending the administration of this preparation and the difficulties encountered in synthetic work in this direction, caused a lapse of interest until the accidental discovery of the antipyretic properties of antipyrine in 1885 and acetanilide in 1888. The simplicity of the structure of the latter, with its valuable medicinal properties attracted the attention of pharmacologists, who undertook a thorough investigation into the relationship between structure and physiological action of acetanilide and phenacetin which was discovered shortly afterwards. As a result, new and valuable products began to follow in quick succession, attracting the attention of the medical profession and of capitalists, until to-day the preparation of synthetic drugs forms one of the most important branches of the coal-tar industry. From the enormous amount of study on the part of pharmacologists and chemists, much valuable data have been collected bearing on the relation existing between chemical structure and physiological action, so that the medicinal action of certain nuclei may, in a measure, be modified to suit the demands of modern medicine. In tracing such relationships, one is struck by the fact that several entirely different nuclei possess the same medicinal properties. for example, the derivatives of aniline (acetanilide, phenacetin), pyrazolone (antipyrine), hydrazine (pyrodine), quinoline (analgene) and salicylic acid (aspirin). That is, these nuclei become antipyretics when suitable side chains are associated with them; under other conditions they become antiseptics. Although the action of substituting groups is in general influenced by their nuclei, yet certain side chains develop latent activities in one direction and others in another, or they may either harm or destroy medicinal action entirely. One should not assume from this that the relationship between structure and physiological action is such that it may be formulated into definite laws, or that definite pharmacophore groups exist analogous to the chromophores of the colours.

The groups that favour or develop the physiological action of a nucleus are chiefly the amino, alkyl, hydroxyl, carbonyl, and halogens. If the physiological action of a nucleus be excessively intensified through, for example, an amino group (aniline), this may be controlled through the introduction of an organic acid radicle (as in acetanilide), avoiding carboxylic and sulphonic acid groups which produce weak or inert compounds. Of primary importance is the deportment of these organic compounds in the human organism, for no inference, as to the manner in which they may split up, can be drawn from laboratory experiments. For example, of two substances differing but slightly in structure, one readily splits up whilst the other is eliminated unchanged. Readily oxidisable bodies like uric acid and creatinine pass through the organism unaltered, whilst succinic acid, not changed by concentrated nitric acid, is consumed to carbon dioxide and water. Through the alkalinity of the intestinal canal as well as of the body fluids, ingested chemicals of this class split up, and their physiological action depends upon the resulting decomposition products. It is upon this fact that the synthetic chemist must base his theories relative to action desired. Sometimes unexpected decomposition takes place in the acid secretions of the stomach and unanticipated effects result; as, for example, malarin, a condensation-product of acetophenone and *p*-phenetidine was theoretically an ideal remedy for migraine, but because of its decomposition in the stomach an unexpected systematic toxic effect from liberated *p*-phenetidine resulted. Many of the modern organic synthetic medicinals possess secondary undesirable or toxic effects, hence it is the aim of the chemist and pharmacologist to so alter the structure of such drugs that they can be placed in the hands of the medical profession and even of the general public. While severe criticisms have been offered on the secondary effects of synthetic drugs, it must not be forgotten that medical authorities frequently subject them to more severe tests than our older and better known remedies can withstand. Caution must always be exercised with remedies involving idiosyncrasies and cumulative effects. A great stimulus to this search after new remedies has been the success attending the study of the structure (chemical and pharmacological) of the alkaloids, which has resulted in the production of compounds from which the objectionable features of the natural products have been, in many cases, eliminated. For examples we have the many local anæsthetics as cocaine substitutes; and the codeine succedaneums as heroin and dionin. The study of the structure of caffeine has given us theophylline and its derivatives; the sedative effects of valerian led to its study and the production of a variety of such compounds as validol, quietol, &c.; the undesirable effects of salicylic acid have given us the aspirin class of derivatives, and so on.

Various methods of classification (chemical and physiological) of the synthetic drugs have been attempted, but none of them is entirely satisfactory. One method classifies the aliphatic derivatives under hypnotics and anæsthetics, and those of the aromatic series under antipyretics and antiseptics; another classification takes up the pharmacology of the various groups, for example, the aliphatic hydroxyls as narcotics, the aromatic phenols as antiseptics, the aromatic amino derivatives as antipyretics, &c. Since the structure and nature of the various nuclei influence largely the pharmacology of these radicles, this method is open to objection. The physiological classification is objectionable to the chemist, since compounds of entirely different structure are arranged under the same heading. In this article the method adopted consists in arranging the compounds into general groups according to their medicinal action; as, for example, antipyretics, hypnotics, antiseptics, &c., the compounds under these groups being classified chemically as far as possible. The object has been to give prominence to the presence of certain nuclei and groupings which occur in each of these classes, and to the influence exerted by the introduction of new radicles or structural changes; in other words, to show, wherever possible, the relationship between chemical constitution and physiological action in comprehensive form. For a more detailed *exposé* of this subject, the following works may be consulted:—

Chemical Basis of Pharmacology, Francis and Brickdale; Einführung in die Pharmakologie, Spiegel; Anleitung zur Beurteilung der neueren Arzneimittel, J. Lipowski; Neuere Arzneimittel, H. Hildebrandt; Die neuesten Arzneimittel, H. Peters; Neue Arzneimittel, G. Arends; New and Nonofficial Remedies, Council of Amer. Med. Assn.; Die Arnzneitherapie der Gegenwart, M. Kahane; Neue Arzneimittel, Lueders; Arzneimittel Synthese, Fraenkel; Chemistry of Synthetic Drugs, Percy May; Merck's Semiannual Reports; Relation between Chemical Constitution and Physiological Action, Jowett and Pyman, 7th and 8th International Congress.

Only the more important of the newer chemicals are given, limiting the list to those bearing copyrighted or specially coined titles. For the extensive list of all possible combinations of medicinal chemicals, the reader is referred to Merck's catalogues. Patent numbers are given wherever obtainable. D. R. P.= German Patent; U.S. Pat.=United States Patent; Eng. Pat.=British Patent. The names of the manufacturers of the various remedies are abbreviated. Most of these products may be obtained from Messrs. Burroughs and Wellcome London; Gehe and Co., of Dresden, N; and G. and R. Fritz, Pezoldt, and Suess, of Vienna.

Aethenstaedt=Aethenstaedt and Redeker, Hemelingen, Germany.

A. G. f. A.=Aktiengesellschaft für Anilinfabrikation, Berlin, O.

Barnes Co.=A. C. Barnes Co., Philadelphia, Pa.

Basel, C. F.=Baseler Chemische Fabrik, Basel.

Bayer=Farbwerke vormals Fr. Bayer und Co., Elberfeld, Germany.

Berlin Lab.=Chem. Lab. Gr. Frankfurter Str. 80, Berlin.

Bibus=Dr. B. Bibus, Vienna, I.

Blaes=J. Blaes Co., Lindau in Baden, Germany.

Boehringer=C. F. Boehringer und Soehne, Waldhof bei Mannheim.

Burroughs=Burroughs Wellcome and Co., London.

Byk=Dr. H. Byk, Windscheid str. 23, Charlottenburg, Germany.

Charlottenburg=Vereinigte Chem. Fabriken in Charlottenburg, Germany.

Cordes=Cordes, Hermanni und Co., Hamburg.

Elb=Max Elb, G. m. b. H. Fabrik, Dresden.

Erdmann=C. Erdmann, Leipzig; Lindeman, Saxony.

Falkenberg=Chem. Fabrik Falkenberg, Gruenau, Berlin.

Feigel=E. Feigel, Lutterbach, Alsace.

Fischer=E. W. Fischer, Boehlitz, Leipzig.

Freund=Freund und Redlich, Berlin.

Fritz=G. und R. Fritz, Petzold und Suess, Vienna.

Fritzsche=Franz Fritzsche Co., Hamburg.

Gans=L. W. Gans, Frankfurt, Germany.

G. C. I. Basel=Gesellschaft für Chem. Industrie, Basel.

Gehe Co.=Gehe Aktiengesellschaft, Dresden.

Guestrow=Dr. Hillringhaus and Heilmann, Guestrow, Germany.

Gloess=P. Gloess, Solothurn, Switzerland.

Helfenberg=Chem. Fab. Helfenberg, Helfenberg, Dresden.

Hell Co.=G. Hell und Co., Troppau, Germany.

Heinemann=Ad. Heinemann, Eberswald, Germany.

Henning=G. F. Henning, Berlin, S.W., 48.

Hoechst=Farbwerke vorm. Meister, Lucius und Bruening, Hoechst a. M., Germany.

Heyden=Chem. Fab. von Heyden, Radebeul, Dresden.

Hillringhaus=Dr. Hillringhaus und Heilmann, Fabrik, Guestrow.

Hofmann=Dr. Hofmann Nachfolger, Merane, Saxony.

Horowitz=Chem. Institute A. Horowitz, Berlin, N. 24.

J. A. W.=J. A. Wuelfing, Berlin, S. W. 48.

Kalle=Kalle und Co., Biebrich on Rhine.

Klopfer=Volmar Klopfer, Leubnitz, Dresden.

Knoll=Knoll und Co., Ludwigshafen on Rhine.

Kohlmeyer=C. K. Kohlmeyer und Co., Berlin, W. 10.

La Zyma=La Zyma, Montreux, Switzerland.

La Roche=Hoffmann La Roche Co., Basel.

Lehmann=Berlin Capsule Fabrik, Lehmann, Berlin.

Leonhardt=Leonhardt Co., Zwickau, Saxony.

Lewinsohn=Chem. Institute Lewinsohn, Berlin, S.W.

Lingner=Chem. Fabrik, Lingner, Dresden, A.

Luedy=Luedy & Co., Burgdorf, Switzerland.

Mallinkrodt (Mkdt.)=Mallinkrodt Chemical Works, St. Louis, U.S.A.

Marquart=Chem. Fabrik Marquart, Beuel on Rhine.

Merck=E. Merck, Darmstadt.

Mulford=A. K. Mulford Co., Philadelphia.

Poehl=Prof. v. Poehl und Soehne, St. Petersburg, Russia.

Poulenc=Poulenc Frères, Paris.

Parke Davis=Parke, Davis und Co., Detroit, Michigan.

Reiherstieg=Chem. Werke, Reiherstieg, Hamburg.

Rhenania=Chem. Fabrik Rhenania, Aachen.

Riedel=J. D. Riedel Akt. Gesellschaft, Berlin, N.

Rump=Rump und Lehners, Hannover.

Sandoz=Sandoz und Co., Basel.

Schering=Chem. Fab. auf Aktien vorm, E. Schering, Berlin.

Schimmel=Schimmel und Co., Leipzig.

Schoetensack=Chem. Fab. vormals Schoetensack, Ludwigshafen.

Schroder=A. Schroder, Landwehr Str. 45, Munich.

Schuchart=Theo. Schuchart, Goerlitz, Germany.

Schuelke=Schuelke & Mayr, Hamburg.

Schuetz=Dr. Schuetz und v. Cloedt, St. Vith on Rhine.

Schulz=Chem. Fab. Fritz Schulz, Leipzig.

Siegfried=B. Siegfried, Zofingen, Switzerland.

Speier=Dr. Speier und Karger, Berlin, N. 54.

Speyer=Speyer und Grund, Frankfurt on Main.

Trommsdorf=H. Trommsdorf, Aachen.

Valentiner=Valentiner und Schwarz, Plagwitz, Leipzig.

Van Gember=Van Gember und Fehlhaber, Weissensee, Berlin.

Voswinkel=Dr. A. Voswinkel, Berlin, W. 57.

Weil=Drs. R. und O. Weil, Frankfurt on Main.

Wolfrum=H. Wolfrum und Co., Augsburg.

Wuelfing=J. A. Wuelfing, Berlin, S.W. 48.

Zimmer=Vereinigte Chininfabriken, Zimmer und Co., Frankfurt on Main.

Hydrocarbons. The aliphatic hydrocarbons possess in general a narcotic action, influencing the central nervous system in gradually paralysing in turn the functions of the brain, spinal cord and medulla oblongata, affecting first the sensibilities as regards external impressions and stimulation. The physiological intensity of these narcotics increases with their carbon content, and the unsaturated hydrocarbons are more active than the saturated compounds of same carbon content. Branched chains, where a number of alkyl groups are linked with a carbon atom, favour narcotic action. This effect is intensified through the introduction of hydroxyls and also halogens in some instances, while in others it is entirely lost. Thus whilst methane is practically free from narcotic effect, the introduction of chlorine develops this action, the intensity increasing with the number of atoms introduced, reaching a maximum in CCl_4. The same holds for the higher homologues, but with the increase in carbon content their relative volatility and absorption possibilities, so essential for inhalation anæsthesia, decrease. The bromine substitution products deport themselves similar to the chlorine derivatives, but are less intense in action owing to lower degree of volatility, whilst the chief iodine derivative (iodoform) is only valuable for local application. The aromatic hydrocarbons, on the other hand, possess but very feeble narcotic properties, their action being chiefly convulsive and paralytic in connection with a well-marked lowering of temperature. Through the influence of substituting groups, their untoward action may be almost entirely eliminated, as exemplified among the antipyretics. The higher homologues of benzene, according to the number and kind of substituting alkyl groups, possess varying toxic action, methyl and ethyl benzene are more toxic whilst methyl *iso*propyl benzene (cymene) is less so than benzene. In general, relative toxicity decreases with the number of alkyl groups introduced, whilst the positions of the substituting groups bear an important part in physiological action. Pharmacologically, the halogens exert very little influence upon the aromatic nuclei.

Hydroxyl groups. The hydroxyl group develops the hypnotic characters of the hydrocarbons, increasing in intensity from the primary to the secondary and tertiary, and with the length of the unbranched chain. While the odour of the lower alcohols is feeble, that of the higher unsaturated alcohols is frequently marked (linalool). With increase in number of hydroxyls, the narcotic effect and odour are replaced by sweet taste. Physiologically, the introduction of the hydroxyl group in the aromatic hydrocarbons develops the property of causing a local caustic action, as seen in the phenols. While benzene affects the brain first and then the spinal cord, the action of phenol is restricted to the latter, exciting the motor centres of the spinal cord, the convulsive action diminishing with the number of hydroxyl groups. Intensity in physiological action depends upon the relative position of the substituting groups, thus with dihydroxybenzenes toxic action increases from the para- to meta- and ortho-derivatives.[1] Through introduction of alkyls in phenol, intensity of antiseptic action increases, while its caustic and convulsive effects diminish (guaiacol), although in cases where other substituting groups are present the alkyloxy group introduces hypnotic characters (phenetidine derivatives). In veratrole (dimethyl ether of pyrocatechol) the undesirable secondary effects of guaiacol are absent, also its desirable effects, because of too great stability; hence the presence of one free hydroxyl group is physiologically desirable (as in guaiacol), or if covered by an acid radicle (duotal, benzosol), practically the same effects are attained with a minimum of secondary action. The closing of the hydroxyl causing an alteration to a complete disappearance of the primary medicinal action of a substance may be illustrated among the tannins, benzyloxy tannin being devoid of astringent properties; less marked yet characteristic are eugenol, anisole, phenetole, pyrogallol methyl ether, resorcinol diethyl ether: compare *Synthetic morphine derivatives.* The alkyl ethers are physiologically hypnotics; this extends to many other compounds containing the ethoxyl group as ethoxycaffeine, phenacetine, &c. The introduction of alkyl groups in the nucleus of phenols increases their antiseptic powers. The same is true of the halogens but to a greater degree, the effect increasing with the number of halogen atoms; this applies to phenols or their ethers. Compounds containing two phenol groups linked together (as in diphenyl or dihydroxydiphenyl methane) exhibit intensified antiseptic properties. If, however, the linking groups be —CO or —SO_2, this action is considerably decreased.

Aldehydes and ketones. Among these compounds, the narcotic effects of the hydrocarbon nuclei increase like those of the alcohols. Owing to the reactive characters of the aldehydes, a great variety of condensation-products have been produced, and only those that readily yield chloral (as chloralamid, chloralose, dormiol, &c.) possess sufficient hypnotic action to be of value. The ketones possess in general, hypnotic properties. Dimethyl ketone (acetone) causes intoxication-hypnosis with accelerated pulse, diethyl ketone and its higher homologues have no such action. Aromatic radicles diminish hypnotic action materially. More profound hypnotics are the ketoximes, in which the duration of sleep increases with the molecular weight of the alkyl group; unfortunately, undesirable secondary effects prevent their use. The influence of the introduction of hydroxyls in the branched carbon chains is the same as with the alcohols, causing complete disappearance of hypnotic action as exemplified in the sugars. The aromatic aldehydes are not particularly toxic when their local irritant action is eliminated: this is due to their rapid oxidation. These bodies play an important part in synthetic perfumery; for example, cinnamic aldehyde, anisic aldehyde, benzaldehyde, phenylacetaldehyde (hyacinth), vanillin, piperonal, citral, &c.

Acids and esters. The introduction of the carboxylic or sulphonic group into compounds of well-defined toxic properties, results in a marked diminution of this action: thus benzene and its derivatives, aniline, naphthalene, phenol, pyridine and quinoline, are far more toxic to the organism than their respective carboxylic derivatives benzoic acid, salicylic acid, naphthalene, pyridine and quinoline carboxylic acids; pyrogallol is far more toxic than gallic acid: the same is true of the corresponding sulphonic acids. Thus symphoral (caffeine sulphonic acid) is purely diuretic; sulphanilic acid is indifferent, and morphine sulphonic acid may be given in large doses without effect.

The first-named poisonous class of aromatic bodies on entering the system, readily submit to oxidation and reduction, giving rise to toxic action, but the relative stability of the carboxyl and sulphonic acid groups and their resistance to processes of oxidation serve to protect the derivatives from further chemical change. Further, the aromatic nitro derivatives lose their toxic effects through introduction of sulphonic or carboxylic groups. The lower aliphatic acids seem to accelerate metabolic processes, particularly intestinal peristaltis. Since they are consumed in the body to carbonic acid, they serve to increase the

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[1] Of the trihydroxybenzenes, phloroglucinol is but slightly toxic and caustic, while pyrogallol is very toxic.

alkalinity of the body fluids, hence are of value in gout and similar disturbances resulting from faulty metabolism. The carboxyl group, *per se*, is not toxic but may become so when combined with another atomic complex; thus glyoxalic acid

$$(\mathrm{OHC{-}COOH})$$

yields oxalic acid in the urine and is toxic; ethylene glycol which likewise yields oxalic acid yet is non-toxic; glyoxal

$$(\mathrm{OHC{-}CHO})$$

which is eliminated unchanged, is very toxic; oxalic acid occurs in urine after ingestion of large amounts of grape sugar. The toxicity of oxalic acid diminishes quickly if methylene groups are inserted between the two carboxyls as in malonic and succinic acids. For further influence of carboxylic groups, see under *Antipyretics*, also *Local Anæsthetics*.

The esterification of the carboxyl group changes it physically and physiologically, usually developing narcotic action in the case of the aliphatic acids. Among these products we find many odorous principles such as the 'fruit essences,' also innumerable synthetic perfumes which also possess a distinct narcotic action, moreover such sedatives as validol and bornyval belong to this class. Particularly odoriferous are the esters of the aromatic acids, as methyl salicylate, anthranilic methyl ester, benzyl benzoate, &c. In addition, these esters play an important part in the development of local anæsthetic action in cocaine, eucaine, orthoform, &c. (*see Local anæsthetics*).

Organic ammonia derivatives. *Aliphatic amines.* The exciting influence of ammonium hydroxide upon the functions of the spinal cord manifests itself in cessation of breathing, convulsion, and finally paralysis of these centres, The intensity of this action is diminished according to the number of alkyl groups introduced (amines), increasing, however, with their molecular weight. With the disappearance of the typical characteristics of ammonia through alkylation, we find another distinctive action developed, especially among the quartenary amines, namely the curari effect. While the narcotic characters of the hydrocarbons disappear when combined with ammonia, we find through introduction of acid radicles (acid amides), this effect reappears, feeble in case of the monobasic acids, increasing in intensity with molecular weight. This action is intensified through the well-known action of halogens, for example, diethyl-, dipropyl-, and ethylpropyl bromacetamide. Notable is the effect of the introduction of alkyl amines (dimethylamine) in antipyrine (pyramidon), which not only intensifies its specific action but also eliminates largely its secondary effects. Of special significance is carbonic acid, considered as formic acid, in which a hydrogen is replaced by OH, this forms two amides, carbamic acid and urea. As may be expected, the alkyl esters of carbamic acid (urethanes) are hypnotics, the intensity of their action increasing with the molecular weight of the alkyl group, any toxic effects being overcome, as is customary, through the introduction of an acetyl radicle in the amino group. The alkylisation of urea does not develop any marked hypnotic action until combined with a dibasic acid radicle, as in barbituric acid (veronal, proponal). The aromatic amines possess such marked antipyretic properties that all possible precautions must be taken to modify their excessive and toxic effects, such as acetylation and alkylation (*see Antipyretics*).

The basicity imparted by the amino acids is employed in preparing soluble compounds of otherwise insoluble derivatives (as phenocoll).

The pharmacodynamic actions of other groups are discussed under the special divisions, *v. Suprarenal preparations.*

ANTIPYRETICS, ANTIRHEUMATICS AND ANTINEURALGICS.

Apart from their medicinal value the organic compounds belonging to this class offer many interesting points in tracing the relationship between chemical structure and pharmacodynamic action. That a number of these substances possess antipyretic, antirheumatic and antineuralgic properties in common may be explained by the close relationship of these diseases, that is, they arise from fundamentally infectious, toxic, or auto-toxic conditions. The majority of the enumerated preparations are derivatives of nuclei possessing a decided toxic action, but by a careful study of the influence of groupings, elimination products and pharmacological structure, primary and secondary toxic effects are more or less eliminated. These latter form the chief difficulties encountered to-day in the preparation of synthetic drugs, for not only must individual idiosyncrasies be considered, but also prolonged medication and possible cumulative effects. Unforeseen difficulties may arise in that a product, which from a chemico-pharmacological standpoint is ideal, may either undergo a too rapid decomposition or an unanticipated splitting up, or prove to be too stable in the human organism, and thereby fail to accomplish its purpose. With this class of remedies, it is desirable, from a pharmaceutical standpoint, to present them in a soluble form. Very few are soluble in water. Attempts to render them soluble through sulphonating or carboxylating usually result in comparatively inert products. The use of amino- acids has not proved successful commercially. One of the best examples of this is phenacetin. A consideration of the many derivatives of *p*-phenetidine serves to show the futility of such attempts. The various groups of antipyretics owe their action to essentially different nuclei, but the general principles governing the action of the side chains remain the same. They may be classed as follows:—

Acetylated amines. With the introduction of alkyl groups into the ammonia molecule, the convulsive action of the latter materially decreases whilst the narcotic effect of the alkyl disappears in a measure, both components neutralising one another. Quite different is the result of the introduction of the convulsive excitant aromatic alkyls: aniline (phenylamine) influences chiefly the motor centres of the midbrain (mesocephalon), producing paralysis of its functions, resulting in vertigo, sleep, and finally collapse. Further, aniline and its homologues destroy the hæmoglobin. Apart from these undesirable symptoms, the aromatic amines produce a marked lowering of the temperature, hence are of value in combating fevers, provided the toxic effects can be sufficiently eliminated. The higher homologues of aniline possess like toxic properties, modified, however, by the position of the substituting group; thus metatoluidine behaves like aniline, whilst the ortho- and paratoluidines are much milder. With an alkyl group, as in benzylamine ($C_6H_5{\cdot}CH_2{\cdot}NH_2$), the anti-pyretic action almost disappears. To eliminate, as far as possible, the accompanying toxic symptoms of the substituted aromatic amines, we usually resort to the introduction of acid radicles, the substitution taking place in the amino group. As a result of the acetylation of the aromatic amines, more stable bodies are produced which are far more resistive to the influences of the circulation. The relative degree of stability increases with the molecular weight of the substituting acid: thus formanilide is more toxic than acetanilide, because of its ready decomposition, while benzanilide is but mildly antipyretic, and valerylanilide inert, being eliminated unchanged from the system. The effect of these anilides are those of aniline, protracted, depending on the relative slowness of their decomposition. If a hydrogen of the methyl group in acetanilide be replaced by COOH, an insoluble, inert, malonanilic acid results. The introduction of a hydroxyl group in the methyl of acetanilide (hydroxyacetanilide), results in no material influence in therapeutic effect. The introduction of a sulphonic acid group in the acetyl group (sulphoacetanilide) or the nucleus (acetyl sulphanilic acid, cosaprin), while giving a more soluble product, results, as previously stated, in diminished potency. If acetanilide's nitrogen be methylated (exalgin $C_6H_5{\cdot}N(CH_3)CO{\cdot}CH_3$), a diminished antipyretic and increased toxic action results. The reverse is the case if the alkyl enters the acid group as in phenylurethane (euphorin $C_6H_5NH{\cdot}CO{\cdot}OC_2H_5$). The popularity of acetanilide may be ascribed more to its use in combination with an alkali bicarbonate with or without caffeine, sold extensively as 'headache powders.'

Acetanilide. Acetyl amino benzene
$C_6H_5NH{\cdot}COCH_3$ m.p. 112°.
Benzanilide. Benzoyl amino benzene
$C_6H_5NH{\cdot}COC_6H_5$ m.p. 160°–162°.
Benzacetine. Acetamino ethoxy salicylate
$C_6H_3(OC_2H_5)(NH{\cdot}COCH_3)COOH$ m.p. 190°.
Cosaprin. Acet-*p*-sulphanilate of sodium
$C_6H_4(NH{\cdot}COCH_3)SO_3Na[1:4]$. La Roche.
Exalgin. Methyl acetanilide
$C_6H_5N(CH_3)CO{\cdot}CH_3$ m.p. 101°. Merck.
Methacetin. Acetanisidine
$C_6H_4(OCH_3)NH{\cdot}COCH_3$ m.p. 127°.

II. **Amino phenols.** Phenacetin, the most popular of all antipyretics in medical practice, owes its introduction to the observation that acetanilide undergoes oxidation in the human organism, whereby a hydroxyl group enters the ring in the para- position to the amino group. *p*-Aminophenol was found to be a powerful antipyretic, much less toxic than aniline yet attacking the blood corpuscles with formation of methaemoglobin. The introduction of an acetyl group (acetyl-*p*-amino phenol) diminished this objectionable feature through greater molecular stability, but not sufficiently until the phenol hydroxyl was covered by an alkyl (ethyl). The chemico-pharmacological structure of phenacetin is such that as yet no improvement has been effected. The methyl derivative (methacetin), possessing a maximum antipyretic effect, is less satisfactory, while the introduction of higher alkyls in the hydroxyl group of acetyl amino phenol produce weak or inert derivatives owing to excessive stability and failure to split off amino phenol. The same may be said of aliphatic groups containing COOH (*e.g.* acetaminophenoxyl acetic acid,

$$C_6H_4(OH)(COOC_6H_4{\cdot}NHCOCH_3).$$

If, on the other hand, an hydroxy acid radicle of the aromatic series replaces the carboxyl hydrogen as in salophen

$$C_6H_4(OH)(COOC_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_3),$$

salicylic acid and aminophenol appear in the urine, hence the anticipated antipyretic action. The toxicity of aniline increases through the introduction of an alkyl radicle in the amoni group, but diminishes if an aryl radicle is introduced, or there be two alkyl groups.[1] Further, the acid radicle entering the amino group and thus diminishing toxicity must not split off through the action of the gastric secretions, or the undesirable effects of *p*-phenetidine will follow; while, on the other hand, the acid radicle should not be too firmly linked or an inert product will result. Formylphenetidine, quite unstable, is irritating; while pyrantin (succinimid phenetidine $C_6H_4(OC_2H_5){\cdot}N[COCH_2]_2$) is inert because of excessive stability; the same applies to *iso*-propyl and *iso*-butyl phenetidine. Only such derivatives of *p*-phenetidine possess an antipyretic action as give the indophenol reaction in the urine, depending on the formation of a red colour upon the addition of nitrous acid followed by beta-napthol. That is, active derivatives of this class must split up into bodies containing a free amino group (phenetidine or amino phenol), the intensity of action depending upon the rapidity of decomposition. The employment of aromatic acids in place of acetic (for the amino group) either diminishes or totally destroys antipyretic action. The urea derivatives of phenetidine possess antipyretic properties, dulcin (ethoxy-phenyl carbamide), an intensely sweet chemical, belongs to this group. Attempts to render phenacetin or derivatives of *p*-phenetidine soluble, through sulphonating (Phesin) and carboxylating [Benzacetine

$$C_6H_3(OC_2H_5)(NH{\cdot}COCH_3)(COOH)$$

the nuclei were unsuccessful medicinally because of their excessive stability. More successful results were attained through the use of the amino acetyl group (phenocoll).

Amygdophenin. Mandelic *p*-phenetidine
$C_6H_4(OC_2H_5){\cdot}NH{\cdot}CO{\cdot}CH(OH)C_6H_5$
m.p. 140·5° Hoechst.
Apolysin. Aconitic monophenetidine
$C_6H_7O_6{\cdot}NH{\cdot}C_6H_4OC_2H_5$
m.p. 72° (D. R. P. 87428) Heyden.
Citrophen. Monophenitidine citrate. m.p. 188°.
Eupyrine. Vanillin-ethyl carbonate-*p*-phenetidine
$C_6H_4(O{\cdot}C_2H_5)N:CH{\cdot}C_6H_3(O{\cdot}CO{\cdot}OC_2H_5)OCH_3$
m.p. 87° (U.S. Pat. 658446) Zimmer.

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[1] If the hydrogen of the amino group in *p*-acetamino-phenetole be replaced by an alkyl, a narcotic is obtained; as, for example, methyl phenacetin

$$(C_6H_4(OC_2H_5)N(CH_3)COCH_3).$$

If an ethyl group enters, a diminished narcotic effect results.

Kyrofin. Methyl glycolic-*p*-phenetidine $CH_3{\cdot}OCH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OC_2H_5$ m.p. 98°, Basel, C. F.

Lactophenin. Lactyl-*p*-phenetidine $C_6H_4(OC_2H_5)NH{\cdot}CO{\cdot}CH(OH)CH_3$ m.p. 118° (U.S. Pat. 503743) Boehringer.

Malakin. Salicyl *p*-phenetidine $C_6H_4(OC_2H_5)NH{\cdot}CO{\cdot}C_6H_4{\cdot}OH+H_2O$ m.p. 92°, G. C. I. Basel.

Malarin. Acetophenone-*p*-phenetidine $C_6H_5C(CH_3){:}N{\cdot}C_6H_4{\cdot}OC_2H_5$ m.p. 88° (D. R. P. 98840) Valentiner.

Phenacetin. Acet-*p*-phenetidine m.p. 134° (U.S. Pat. 400086), Bayer.

Phenocoll. Amino-acet-*p*-phenetidine $(C_6H_4(OC_2H_5)NH{\cdot}CO{\cdot}CH_2NH_2)HCl$ m.p. 95°. Anhydrous base 100·5° (U.S. Pat. 543214) Schering.

Phenosol. Salicyloacetate of *p*-phenetidine m.p. 182°, Hofmann.

Pyrantin. *p*-Ethoxy-phenyl-succinimid $[CH_2{\cdot}CO]_2N{\cdot}C_6H_4{\cdot}OC_2H_5$ m.p. 155°, Hoechst.

Salophen. Acetyl *p*-aminophenol salicylate $C_6H_4(OH)(COOC_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_3)$ m.p. 188° (D. R. PP. 62533, 62289) Bayer.

Thermodin. Phenacetin urethane $C_6H_4(OC_2H_5){\cdot}N(COOC_2H_5){\cdot}COCH_3$ m.p. 86°–88°, Merck.

Triphenin. Propionyl *p*-phenetidine $C_6H_4(OC_2H_5)NH(CO{\cdot}CH_2{\cdot}CH_3)$ m.p. 120° (U. S. Pat. 535846) Merck.

Valerydin. Valeryl *p*-phenetidine $C_6H_4(OC_2H_5)NH{\cdot}C_5H_9O$ Erdmann.

Vinopyrin. *p*-Phenetidine tartrate m.p. 168°, Fischer.

III. **Salicylic acid derivatives** (*for internal use*). As is well known, the introduction of a COOH group into compounds of well-defined toxic or antiseptic properties results in a marked diminution of these properties. Particularly is this the case with the phenol acids (salicylic), the ortho-derivative being more toxic and antiseptic than benzoic acid and much less so than phenol. To-day, salicylic acid is one of the most important of our medicinal chemicals. Owing, however, to its irritant action and consequent gastric disturbances with frequent tinnitis, we find that the majority of the newer derivatives consist of compounds designed to split up in the intestinal tract only. This is usually accomplished through acylation of the OH group or esterification of the COOH group as typified in aspirin and glycosal. Some of the combinations are more especially designed for intestinal disinfection as alphol, salacetol, cordol, &c.

Alphol. *a*-Naphthyl salicylate $C_6H_4(OH)COOC_{10}H_7$ m.p. 83°.

Aspirin. Acetyl salicylic acid $CH_3{\cdot}COO{\cdot}C_6H_4{\cdot}COOH$ m.p. 135° (U. S. Pat. 644077) Bayer.

Aspirin, soluble. The calcium salt of aspirin; readily soluble and produces no gastric disturbances.

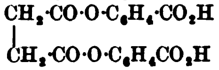
Benzosalin. Benzoyl salicylic methyl ester $C_6H_5COO{\cdot}C_6H_4{\cdot}COOCH_3$ m.p. 85° (D. R. P. 169247), La Roche.

Betol. *β*-Naphthyl salicylate $C_6H_4(OH)COOC_{10}H_7$ m.p. 95°.

Benzacetin. Acetamino-ethyl salicylic acid $C_2H_5O{\cdot}C_6H_3(NHCOCH_3)COOH$ m.p. 205°.

Cordol. Tribromosalol $C_6H_4(OH)COO{\cdot}C_6H_2Br_3$ m.p. 195°.

Diaspirin. Succinyl salicylic acid



$$\begin{array}{l} CH_2{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H \\ | \\ CH_2{\cdot}CO{\cdot}O{\cdot}C_6H_4CO_2H \end{array}$$

m.p. 176°–180° (D. R. P. 196634), Bayer.

Diplosal. Salicylo-salicylic acid $OH{\cdot}C_6H_4{\cdot}COO{\cdot}C_6H_4COOH$ m.p. 147°, Boehringer.

Glycosal. Monosalicylic glyceryl ester $C_6H_4(OH)COO{\cdot}C_3H_5(OH)_2$ m.p. 71° (D. R. P. 127139), Merck.

Indoform. Salicylic methylene acetate m.p. 108°, Schulz.

Methylaspirin. Methyl acetylsalicylate $CH_3{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}COOCH_3$ m.p. 54°, Merck.

Novaspirin. Methylene citro-salicylic acid (D. R. P. 185800), m.p. 150° Bayer.

Salacetol. Acetonyl salicylate $C_6H_4(OH)COO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$ m.p. 71°, Schoetensack.

Salibromin. Dibromsalicylic methyl ester $C_6H_2Br_2(OH)COOCH_3$ Heyden.

Salicreol. Creosote salicylate

Salol. Phenyl salicylate $HO{\cdot}C_6H_4{\cdot}COOC_6H_5$ m.p. 43°

Vesipyrin. Phenyl acetylsalicylate $C_6H_4(OCOCH_3)COOC_6H_5$ Reiherstieg.

For external use. Another method for the employment of salicylic acid, either alone or in conjunction with its internal use, consists in the local application of its various esters. These must be either in fluid form or, if solid, soluble in fats, so that absorption by the skin may readily take place. Owing to the objectionable odour of oil of wintergreen, various other inodorous esters of the aliphatic series have come into use.

Mesotan (ericin). Salicylic methoxymethyl ester $C_6H_4(OH)COOCH_2{\cdot}OCH_3$ b.p. 162° (42 mm.) (D. R. P. 137585) Bayer.

Protosal. Salicylic glycerol formal ester b.p. 200° (12 mm.) (D. R. P. 163518) Schering.

Saligallol. Pyrogallol disalicylate m.p. 141°, Knoll.

Salimenthol. Menthyl salicylate (D. R. P. 171453), Bibus.

Salit. Borneol salicylate $C_{10}H_{17}O{\cdot}CO{\cdot}C_6H_4{\cdot}OH$ (D. R. P. 175097), Heyden.

Spirosal. Salicylic monoglycol ester $C_6H_4(OH){\cdot}COO{\cdot}CH_2{\cdot}CH_2OH$ b.p. 170° (12 mm.) (D. R. P. 164128), Bayer.

IV. **Quinine derivatives.** Quinine will always retain its popularity as an antifebrile, chiefly because of the total absence of any depressing action upon the heart. Its bitter taste and what few secondary effects it may produce, as tinnitis and quinine intoxication, have been largely overcome in a number of new derivatives of real merit. These are esters in which the hydroxyl hydrogen of quinine has been replaced by carbonic acid (aristochin), phenyl carbonic acid (euchinin), salicylic acid (salichinin), &c.

Aristochin. Diquinine carbonic ester $CO(O{\cdot}C_{20}H_{23}N_2O)_2$ m.p. 189° (U.S. Pat. 625075), Bayer.

Bromochinol. Acid dibromsalicylate of quinine $C_{20}H_{24}N_2O_2{\cdot}2[C_6H_2Br_2(OH)COOH]$ m.p. 198°, Zimmer

Chinaphenin. Phenetidine quinine carbonic ester $CO(NH\cdot C_6H_4\cdot OC_2H_5)(C_{20}H_{23}N_2O_2)$ (D. R. P. 109259), Bayer.

Chinaphthol. Quinine beta-naphtholmonosulphonate $(C_{20}H_{24}N_2O_2)(C_{10}H_6(OH)SO_3H)_2$ m.p. 185°, Merck.

Euchinin (euquinine). Quinine ethyl carbonate $C_2H_5O\cdot CO\cdot OC_{20}H_{23}N_2O$ m.p. 95° (U. S. Pat. 585068), Zimmer.

Insipin. Diglycollic ester of quinine sulphate $O(CH_2\cdot COO\cdot C_{20}H_{23}N_2O)_2\cdot H_2SO_4,3H_2O$ tasteless. Merck.

Quinine lygosinate. Dioxy-dibenzal-acetone quinine $CO(CH{:}CH\cdot C_6H_4\cdot C_{20}H_{24}N_2O_2)_2$ m.p. 114°, Zimmer.

Rheumatin. Salicylate of salochinin, m.p. 183°.

Salochinin. Quinine salicylic ester $C_6H_4\cdot OH\cdot COO(C_{20}H_{23}N_2O)$ m.p. 141° (U. S. Pat. 678401), Bayer.

V. **Quinoline derivatives.** The earlier attempts to determine the origin of the physiological action of quinine indicated that the quinoline nucleus (tetra hydroquinoline) was largely responsible. While this possesses an antiseptic and antipyretic action, the latter is much weaker and less reliable than that of quinine. In malaria quinoline is inert. The introduction of a methyl group increases its antiseptic effect and diminishes antipyretic action, whilst the methoxyl, as in *p*-methoxy tetrahydroquinoline (thalline), is markedly antipyretic. Owing to its injurious action upon the kidneys, the use of thalline was soon discontinued. A like course followed the introduction of the kairins, methyl and ethyl derivatives of orthohydroxyquinoline tetrahydride. The untoward effects of these remedies (toxic to red blood corpuscles) were not altered either through the introduction of other alkyls or acid radicles in the imido group. Quite different results were obtained by placing ethoxyl and acylamino groups in the positions 1 : 4 (analgene), analogous to phenacetin. More successful derivatives of the class of hydroxyquinolines are found among the antiseptics as loretin, $C_9NH_4I(OH)SO_3H$ diaptherin.

Analgene. *o*-Ethoxy-ana-benzoylamino-quinoline $C_9NH_5(OC_2H_5)NH\cdot COC_6H_5$ m.p. 208°, Bayer.

Chinosol. Hydroxyquinoline potassium sulphate $(C_9H_7ON)_2H_2SO_4$ m.p. 175°–177·5° (U. S. Pat. 906918), Fritsche.

Diaphtherin. Hydroxyquinaseptol $(C_9NH_6\cdot OH)_2C_6H_4(OH)SO_3H$ m.p. 85°, Hoechst.

Quite different results have been attained through the introduction of a carboxylic group into the nucleus or its methylated derivative; such compounds possess not only analgesic action but also are of particular value in uric acid diathesis.

Atophan. 2-Phenylquinoline-4-carboxylic acid $C_9NH_5(C_6H_5)COOH$ m.p. 208–209°, Schering.

Novatophan. Ethyl 6-methyl-2-phenylquinoline-4-carboxylate $C_6H_5\cdot C_9NH_4(CH_3)COOC_2H_5$ m.p. 76° (U. S. Pat. 1045, 759), Schering.

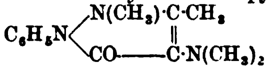
VI. **Pyrazolone derivatives.** Two erroneous assumptions led to the discovery of this group of antipyretics, namely, that quinine was a tetrahydroquinoline derivative and that what is now known as antipyrine was related to this same ring system. Knorr, in 1884, obtained a condensation-product of phenyl hydrazine (antipyretic but toxic) and aceto-acetic ester, the resulting phenyl methyl pyrazolone, was unsuited for therapeutic purposes. Utilising Filehne's previous experiences with substances of like physiological action derived from quinoline, namely kairine and kairoline, a methyl group was introduced which resulted in the formation of the well-known antipyrine. While this substance does not possess any of the antiperiodic properties of quinine, it has greater antipyretic and antineuralgic effects; in general, its action resembles that of salicylic acid. Phenyl monomethyl pyrazolone is only slightly antipyretic. The presence of an aromatic group (like tolyl in tolylpyrine) while not being absolutely essential increases the efficiency. A great improvement over antipyrine in intensity (3 times), mildness and duration of action was attained through the introduction of a dimethylamino group ($N(CH_3)_2$) in place of the only replaceable hydrogen of the nucleus (pyramidone). The success attending the introduction of pyramidone led to a variety of combinations with camphor, salicylic acid, &c., none of which offers any material advantages.

Acopyrin (acetopyrin). Antipyrine acetyl salicylate m.p. 63°/65°, Heyden.

Ferropyrin $(C_{11}H_{12}N_2O)_3(FeCl_3)_2$ (U. S. Pat. 548352), Knoll.

Melrubin. Sodium 1-phenyl 2 : 3-dimethylpyrazolone-4-aminomethane sulphonate $C_{11}H_{11}N_2O\cdot NH\cdot CH_2SO_3Na$ Hoechst.

Pyramidone. Dimethylamino antipyrine



$$C_6H_5N\left\langle\begin{array}{l}N(CH_3)\cdot C\cdot CH_3\\ \qquad\qquad\quad\|\\ CO\text{———}C\cdot N(CH_3)_2\end{array}\right.$$

m.p. 108° (U. S. Pat. 579412), Hoechst.

Pyramidone neutral camphorate, m.p. 80°–90° (U. S. Pat. 686998), Hoechst.

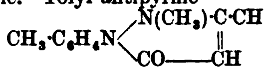
Pyramidone acid camphorate, m.p. 84°–94° (U. S. Pat. 686999), Hoechst.

Pyramidone salicylate camphorate, m.p. 68°–70° (U. S. Pat. 680278), Hoechst.

Pyrosal. Acid salicylo-aceto antipyrine, m.p. 150°, Hoffmann.

Salipyrine. Antipyrine salicylate m.p. 92° (U. S. Pat. 444004), Riedel.

Tolypyrine. Tolyl antipyrine



$$CH_3\cdot C_6H_4N\left\langle\begin{array}{l}N(CH_3)\cdot C\cdot CH_3\\ \qquad\qquad\quad\|\\ CO\text{———}CH\end{array}\right.$$

m.p. 137°, Riedel.

Tolysal. Tolypyrine salicylate, m.p. 102°, Riedel.

Trigemin. Dimethylamino antipyrine butyl chloral hydrate, m.p. 85° (D. R. P. 150799), Hoechst.

Tussol. Antipyrine mandelate $C_{11}H_{12}N_2O\cdot C_6H_5\cdot CH\cdot OH\cdot COOH$ m.p. 53° (U. S. Pat. 569415), Hoechst.

VII. **Hydrazine derivatives.** The nucleus of this class, hydrazine or diamide (H_2N-NH_2) is far more toxic than ammonia. Salts of hydrazine produce a condition of excitation followed by depression and coma with irregular pulse. Introduction of acyl groups decreases toxic action. Phenylhydrazine is a strong poison for connective tissue and hæmaglobin. Still more toxic, yet accompanied by a marked antipyretic effect, is the mono-acetyl compound (hydracetin) and laevulic acid phenylhydrazone (antithermin). Therapeutically better adapted with but minor secondary effects are the aromatic semi-carbazides, namely *m*-tolylhydrazide carbonate or *m*-tolyl semi-carbazide (maretin) and *m*-benzamido semi-carbazide (cryogenin).

Antithermin. Laevulic acid phenylhydrazone
$C_6H_5{\cdot}HN{\cdot}N:C(CH_3)CH_2{\cdot}CH_2{\cdot}COOH$
m.p. 108°.

Hydracetin (pyrodin) acetyl-phenylhydrazine
$C_6H_5{\cdot}NH{\cdot}NH{\cdot}COCH_3$
m.p. 128°, Merck.

Agathin. Salicylaldehyde methylphenylhydrazone $C_6H_5(CH_3)N{\cdot}N:CH{\cdot}C_6H_4{\cdot}OH$
m.p. 74°, Hoechst.

Maretin. *m*-Tolyl-hydrazid-carbamate
$CH_3{\cdot}C_6H_4NH{\cdot}NH{\cdot}CONH_2$
m.p. 184°, Bayer.

VIII. **Urethane derivatives.** It has been noted that the toxic action of aniline or the amino phenols is eliminated by the introduction of carboxyl and alkyl groups in different positions. It has been found that the hypnotic urethanes fulfil these conditions when coupled with a phenyl group, losing, however, their hypnotic characters through change in their structure. These compounds are more especially analgesics (*see Carbonic acid derivatives*).

Euphorine. Ethyl phenylcarbamate
$CO(HN{\cdot}C_6H_5)(OC_2H_5)$
m.p. 50°, Heyden.

Neurodine. *p*-Acetoxyphenyl urethane
$C_6H_4(OCOCH_3)NH{\cdot}COOC_2H_5$
m.p. 87°, Merck.

Thermodine. Phenacetin urethane
$C_6H_4(OC_2H_5){\cdot}N(CO{\cdot}OC_2H_5)(CH_3CO)$
m.p. 86°–88°, Merck.

Kyrogenin. *m*-Benzamino semi-carbazide
$C_6H_4(C{\cdot}CO{\cdot}NH_2)(C{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2)$

HYPNOTICS.

Owing to our lack of knowledge concerning the physiology of sleep and possible chemical processes that take place, we are equally ignorant of the exact manner in which sleep is produced by hypnotics. In effect, we must distinguish between narcotics (represented by opium), which produce unconsciousness by intoxication, and the true hypnotics (represented by chloral), in which the sleep is apparently normal. In view of the fact that the sleep produced by the opium class is often attended with undesirable by-effects, and that during their prolonged administration the element of habituation must always be considered, they have been reserved for cases of insomnia due to severe pain, and have been largely replaced in other forms of sleeplessness by the synthetic hypnotics. While this latter class approach the normal conditions, yet the ideal hypnotic remains to be discovered. This must act upon the nerve centres followed later by the most automatic and stable centres, avoiding any profound influence on the respiratory or circulatory centres. Elimination must be rapid and complete leaving no trace of cumulative or secondary action such as digestive disturbances, headache, &c. Well known is the hypnotic effect of the aliphatic hydrocarbons, developed through the introduction of hydroxyl groups (alcohols). That the hydroxyl group serves no further purpose than an anchoring medium is proved by the inert properties of the polyhydric alcohols. That the ethyl group produces a profound hypnotic effect, as in alcohol, is further demonstrated by the decomposition of chloral in the blood to trichlorethyl alcohol, and the necessary presence of alkyl groups in the most important classes of hypnotics. The introduction of the ethoxyl group into caffeine imparts a narcotic effect. It can be said in general that the alkyl groups, more especially the ethyl, possess a distinctive sedative action upon the nervous system. The methyl group generally eliminates or diminishes hypnotic action when associated with an ethyl or propyl group; the propyl radicle with other higher radicles increases the intensity and also toxicity, while their corresponding *iso* groups generally diminish this. Sulphur replacing oxygen contributes to toxicity. The alkyl radicles do not carry hypnotic or sedative action under all conditions; it is only the association of certain groups or nuclei or their structural environment that determines this action. The presence of a sulphonic or carboxyl group inhibits physiological action, and diminishes toxicity. Another factor is insolubility, that is, failure to break down in the system: thus tetronal, which, theoretically, should possess a more profound hypnotic action than trional, is practically inert. A further insight is gained on studying the groups.

Alcohols. The primary alcohols are less narcotic than the secondary and these less so than the tertiary. The longer the carbon chain the more potent the alcohol; if more than one hydroxyl is present, narcotic effect disappears in proportion. In tertiary alcohols, the physiological action depends upon the alkyl groups linked to the tertiary carbon, if the methyl radicle be present, as in trimethyl carbinol (tertiary butyl alcohol), the action is relatively feeble: with ethyl groups, it increases in proportion to the number of such groups united to the tertiary carbon (*see Hydroxyl groups.*)

Amylene hydrate $C_2H_5{\cdot}C(CH_3)_2OH$-dimethyl ethyl carbinol, b.p. 99°–100°. The introduction of halogens into the hydrocarbons increases hypnotic action, as is shown in methyl chloride and chloroform. A similar effect is attained in:

Isopral, $CCl_3{\cdot}CH(CH_3){\cdot}OH$, trichlor-*iso*propyl alcohol (D. R. P. 151545), m.p. 49°, Bayer.

Brometone, tertiary-tribrom-butyl alcohol. Parke Davis $CBr_3{\cdot}C(OH)(CH_3)_2$, m.p. 167°.

Ethers. Methylal (formal) Methylen-dimethyl ether, $CH_2(OCH_3)_2$, b.p. 42°.

Aldehydes. Acetaldehyde is slightly hypnotic; much more so is its polymeride, paraldehyde. The aldols and acetals (ethylidene diethyl ether) possess a mild effect. The further introduction of alcohol groups as in sugar give inert compounds. As cited under the alcohols, the introduction of chlorine or bromine produces a marked increase in hypnotic effect exemplified in chloral, the first synthetic drug. This breaks down in the blood into urochloralic acid, a compound of trichlorethyl alcohol and glycuronic acid. To eliminate the secondary irritant action due to the aldehyde group, various combinations have been introduced. The corresponding bromine derivatives possess a toxic secondary action, whilst those containing iodine are inert. The following chloral combinations exhibit the same effects as chloral on the heart and respiration without an irritant effect on the stomach since they split up in the intestinal tract.

Chloralamide, $CCl_3{\cdot}CH(OH){\cdot}NH{\cdot}CHO$, chloral formamide, m.p. 115° (D. R. P. 50536), Schering.

Chloralimide, $CCl_3CH{:}NH$, m.p. 155°.

Dormiol, $CCl_3{\cdot}CH(OH){\cdot}O{\cdot}C(CH_3)_2C_2H_5$, dimethyl-ethyl carbinol-chloral (D. R. P. 99469), Kalle.

Hypnal, Chloral-hydrate-antipyrine, m.p. 67°, Hoechst.

Butyl-hypnal, Butylchloral-antipyrine, m.p. 70°.

Aromatic aldehydes are usually of low toxicity since they oxidise to inert acids.

Ketones. The action of these, like the alcohols, is governed by their alkyl groups. Dimethyl ketone produces intoxication, stimulation of heart's action, followed by paralysis of the central nervous system, whilst the diethyl and dipropyl ketones are mild hypnotics, free from action on the heart. In general, the aromatic ketones are only slightly hypnotic, while the mixed aromatic and aliphatic ketones are markedly so.

Hypnone $C_6H_5CO{\cdot}CH_3$, phenyl methyl ketone, b.p. 198°–200°.

Sulphonal group. This group was first studied, medicinally, by Baumann and Kast in 1886–1889. They are obtained by oxidising the condensation products of ketones and mercaptans and contain the basic group $>C<\begin{smallmatrix}SO_2-\\SO_2-\end{smallmatrix}$, which carries the hypnotic radicles in the form of methyl and ethyl groups. Only those disulphones which contain ethyl groups are active, and the intensity of effect depends upon the number of such groups contained in the molecule. This reaches its limit, however, in 'tetronal,' which contains four ethyl groups and because of its insolubility fails to break down in the system, and hence is almost inert.

Sulphonal $(CH_3)_2C(SO_2C_2H_5)_2$, diethylsulphone-dimethyl-methane, m.p. 125·6°, Bayer.

Trional $CH_3(C_2H_5){\cdot}C(SO_2C_2H_5)_2$, diethylsulphone-methyl-ethyl-methane, m.p. 76°, Bayer.

Carbonic acid derivatives. The hypnotics under this heading may be classed as derivatives of carbonic acid, carbamic acid and urea. From carbonic acid, no narcotic action can be expected, since the free carboxyl group is toxic. On the other hand, the esters of carbamic acid (urethanes), have the advantage that so long as the doses are not excessive, important life functions are not disturbed. Any toxic action, as collapse or feeble heart action, may be corrected through the introduction of an acetyl group. Hypnotic action is intensified through increase in size of the alkyl group. Urea is inert when an amino hydrogen is replaced by an alkyl group, the product exhibits the action of the latter. Derivatives with primary alkyls are inert; tertiary butyl urea is feebly hypnotic; tertiary amyl urea is stronger, whilst the tertiary heptyl urea is still more active. If both amino groups are replaced symmetrically by such radicles, medicinal action ceases, owing probably to excessive stability.

Adalin. Monobromodiethyl acetyl urea $(C_2H_5)_2CBr{\cdot}CO{\cdot}NH{\cdot}CONH_2$ m.p. 116° (U. S. Pat. 983425), Bayer.

Bromural, monobrom-*iso*valeryl-urea $(CH_3)_2CH{\cdot}CHBr{\cdot}NH{\cdot}CO{\cdot}NH_2$ m.p. 145° (U. S. Pat. 914518), Knoll.

Urethane group. The urethanes (carbamic acid esters), once quite popular, have given way to the sulphonal and barbituric acid derivatives. The latter were introduced by Schmiedeberg in 1885.

Urethane $CO(NH_2)OC_2H_5$, carbamic acid ethyl ester, m.p. 48°–50°.

Hedonal $CO(NH_2)O{\cdot}CH(CH_3)C_3H_7$, methyl-propyl-carbinol-urethane, m.p. 76°, b.p. 215° (U. S. Pat. 659202), Bayer.

Alendrin. The carbamic acid ester of *aa*-dichloro*iso*propyl alcohol $(CH_2Cl)_2CH{\cdot}O{\cdot}CONH_2$ m.p. 82°.

Aponol, $NH_2{\cdot}CO{\cdot}O{\cdot}C(CH_3)_2(C_2H_5)$. Amyl carbamate. Zimmer.

Although hypnotic action is obtained by associating ethyl groups directly with carbon, diethyl acetic and malonic acids are found to be inert, likewise their corresponding amides. This is due to the failure to replace all replaceable hydrogens of the carbon (in tertiary form). This is demonstrated by introducing a (sedative) bromine into diethyl acetamide, thus:

Neuronal $(C_2H_5)_2C(Br)CONH_2$, diethylbromacetamide, m.p. 66°, Kalle.

Malonyl urea derivatives, $CH_2<\begin{smallmatrix}CO{\cdot}NH\\CO{\cdot}NH\end{smallmatrix}>CO$

Neither malonic acid nor its amide possess hypnotic action. The introduction of two methyl groups into the latter is without effect, and one methyl and one ethyl imparts a mild hypnotic action; marked, however, is that produced through the presence of two ethyls, as in:

Veronal $(C_2H_5)_2C<\begin{smallmatrix}CO{\cdot}NH\\CO{\cdot}NH\end{smallmatrix}>CO$, diethyl malonyl urea, m.p. 188° (U. S. Pat. 782739), Merck and Bayer. This very popular hypnotic is furnished in the form of its soluble sodium salt (medinal). The introduction of the propyl radicle increases the duration of the hypnotic effect, whilst *iso*butyl and *iso*amyl radicles, diminish this. A substitution of the imide hydrogens of veronal by alkyls as well as that of oxygen by sulphur yield toxic bodies.

A mixture of 2 parts of codeine diethylmalonylurea with one part of the sodium salt is used as sedative and hypnotic—*Codeonal* (D. R. P. 239323). Knoll.

Chineonal. A compound of veronal and quinine which fuses at 132°. Used in infectious fevers, also as an analgesic. Merck.

Proponal $(C_3H_7)_2C<\begin{smallmatrix}CO{\cdot}NH\\CO{\cdot}NH\end{smallmatrix}>CO$, dipropyl malonyl urea, m.p. 145°, Merck and Bayer. The hypnotic nucleus of these substances is evidently the urea radicle —HN·CO·NH— when present in the cyclic form as a ureide; any change in the barbituric acid ring destroys the hypnotic action.

Luminal $C_6H_5{\cdot}C{\cdot}C_2H_5[CO{\cdot}NH]_2CO$, phenyl-ethyl-malonylurea. Veronal in which an ethyl is replaced by a phenyl group. Stronger hypnotic (U. S. Pat. 1051, 586). Bayer, Merck.

SEDATIVES.

This group serves to reduce nervous hypersensibility as an aid in the general systematic treatment of diseases of the nervous system. According to the specific purpose for which these drugs are used, they may be divided into three classes, namely bromine combinations, valeric acid esters, and derivatives of morphine.

Bromine combinations. When it is necessary to subject the system for a considerable period to the action of bromine and to avoid the undesirable secondary effects such as usually accompany the prolonged use of the alkali bromides, recourse may be had to the brominated fatty and albuminoid bodies. The decomposition of these derivatives usually takes place in the intestinal tract.

Bromipin. Bromine addition-product of sesame oil containing 10 and 33⅓ p.c. of bromine (D. R. P. 96495), Merck.

Bromlecithin. Brominated lecithin containing about 30 p.c. of bromine (D. R. P. 156110), A. G. f. A.

Bromalbacid. Brominated albumin, 6 p.c. bromine, Gans.

Bromochinol. Quinine dibromosalicylate, m.p. 197°, Zimmer.

Bromglidine. Brominated vegetable glidin, Klopfer.

Bromocoll. A brom-tannin-gelatin, 20 p.c. bromine, A. G. f. A.

Bromolein. Brominated unsat. fatty acids of almond oil, 20 p.c. bromine.

Lipobromol. Brominated poppyseed oil, 33 p.c. bromien.

Sabromin. Calcium dibrombehenate, 29 p.c. bromine, Bayer.

Valeric acid derivatives. The replacement of a carboxyl hydrogen by alkyl radicles produces a distinctive narcotic effect, as instanced by ethyl acetate. Here it is evident that the acid radicle remains indifferent, while, on the other hand, the natural and synthetic esters of valeric acid exhibit the sedative effects of both groups. The well-known sedative action of valerian is due chiefly to the presence of the borneol ester of *iso*-valeric acid now sold as:

Bornyval. Bornyl *iso*valerate, b.p. 255°–260°, Riedel.

Bornyval, New. Bornyl *iso*valerylglycollate

$(CH_3)_2CH{\cdot}CH_2{\cdot}COO{\cdot}CH_2{\cdot}COO{\cdot}C_{10}H_{17}$

b.p. 181°/12 mm. Reidel.

Brophenin. Brom-*iso*valerylphenocoll. A brominated phenetidine derivative.

Brovalol. Bornylbromovalerate

$CH_3{\cdot}CH(CH_3)CHBr{\cdot}COO(C_{10}H_{17})$

b.p. 163° (10 mm.) (U. S. Pat. 930504), Schering.

Eubornyl. *a*-Brom-*iso*valeric-borneol ester, Luedy.

Gynoval. *Iso*borneol ester of *iso*valeric acid, b.p. 132°–138°/12 mm., Bayer.

Iodival. ono-iodo-*iso*valeryl urea, m.p. 180° (D. R. P. 197648), Knoll.

Quietol. Hydrobromide of dimethylamino-dimethyl *iso*valeryl propyl ester, m.p. 105°–110°, when pure, 118°, Poulenc.

Validol. Menthol valerate; 30 p.c. free menthol, Zimmer.

Valisan. Borneol-bromo-*iso*valerate, Schering.

Valyl. Valeric diethylamide

$C_4H_9{\cdot}CO{\cdot}N(C_2H_5)_2$

b.p. 210° (U. S. Pat. 897730), Hoechst.

Synthetic morphine derivatives. The hydroxyl groups are intimately associated with the toxic action of morphine, which, through its narcotic characters, differs from all other opium alkaloids, its action being chiefly upon the nerve centres of the brain. Upon closing these OH groups by substituting one or both of the hydrogens by alkyl or acyl radicles, the narcotic characters disappear, while, on the other hand, a spinal excitant (tetanic action) is developed, increasing with the number of alkyls introduced. Thus, codeine produces, like morphine (but in lesser degree), narcosis, followed by an elevated reflex, which, if the dose be sufficiently large, develops tetanic convulsions. Other morphine esters, as codethyline $C_{17}H_{17}ON(OH)OC_2H_5$), and thebaine $C_{17}H_{15}(OCH_3)_2NO$, the latter of which is the most toxic alkaloid of opium, are characterised by their action on the spinal cord, the tetanic effects being identical with those produced by strychnine. This action increases with the number and molecular weight of the alkyl groups introduced; hence codethyline with its ethyl group is more intense in action than codeine, which contains but one methyl group. The same may be said of the acyl compounds, those containing two such radicles are distinctly tetanic in action.

Among all possible derivatives, it is immaterial as to whether an acyl or alkyl radicle, aliphatic or aromatic, is introduced, there is practically no qualitative difference in action so long as the same hydrogen is replaced. The more readily the acid or alkyl group splits off from the nucleus, the closer the properties of the derivative resemble those of morphine. On the other hand, too great a stability produces relatively inert bodies, morphine hydroxy-acetic, propionic or butyric acids are pharmacologically inactive, whereas, on the other hand, the methyl and ethyl esters of these acid derivatives produce intense picrotoxin-like convulsions, the seat of action being the *crura cerebri*.

Winternitz[1] has shown that codeine and dionine produce no effect upon respiration, whilst the introduction of acid radicles increase the respiratory influence of morphine.

In all instances, the narcotic action of morphine is very much diminished, while the tetanic and also the action on the motor nerves is increased. The morphine derivatives of the codeine type, while less active in relieving pain, exert a sedative effect on the unstriped muscles of the bronchi and reduce the disposition to cough; hence are of value in phthisis, bronchitis, asthma, &c.

Dionine. Morphine ethyl ether hydrochloride

$C_{17}H_{17}NO(OH)OC_2H_5.HCl+H_2O$

m.p. 123°–125° (D. R. P. 108075), Merck.

Heroin. Diacetyl morphine hydrochloride

$C_{17}H_{17}NO(O{\cdot}COCH_3)_2{\cdot}HCl$

m.p. 230°–231°, Bayer.

Peronin. Morphine benzyl ether hydrochloride

$C_{17}H_{17}NO(OH)O{\cdot}CH_2{\cdot}C_6H_5{\cdot}HCl$ Merck.

Morphosan. Morphine methylbromide, m.p. 265°,

$C_{17}H_{19}O_3N(CH_3)Br+H_2O$

(D. R. P. 165898, 191088), Riedel Co.

Knorr's[2] investigations have demonstrated the presence of a phenanthrene and a morpholine (oxazine) nuclei to be the basic ring structure of morphine. Assuming that either one or the other of these rings might be the carrier of its physiological action, Knorr prepared a naphthalan-morpholine and methylated the imid hydrogen (methyl morphimetin); the product was

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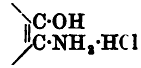
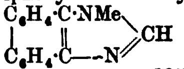
[1] Therap. Monatsh, 1899. [2] Knorr, Ber. 27, 1144.

found to be inert. Vahlen[1] assuming the phenanthrene nucleus to be active centre, prepared morphigenine (hydrochloride of 9-amino-10-hydroxy-phenanthrene)



and found that it had marked narcotic properties. The amidazole derivative of this, resembling morphine and codeine in its effects, was called :—

Epiosin, 4 : 5-diphenylene-1-methylimazole



m.p. 195°, Heinemann.

ANTISEPTICS AND DISINFECTANTS.[2]

Antiseptics are certain chemicals which have the power, in small quantities, to prevent infection or to arrest the multiplication of bacteria, and should be free from harmful action upon the human organism. Disinfectants destroy bacterial life and the noxious properties of putrefactive or fermentative products. Usually, small quantities of these chemicals are antiseptic, and large amounts disinfectant, in their effects.

The great variety of bacterial life, the kind, state, extent, composition, quantity, and condition of the associated matter, together with the difficulty of fixing, inhibiting and sterilising doses of disinfectants, makes the subject of standardisation of disinfectants perplexing and difficult. An ideal disinfectant must be able to destroy bacteria, be harmless to the human organism, penetrative, free from local irritation, toxic action and disagreeable odour. Very few, if any, of the disinfectants are adapted for universal use because of the great variety of conditions presented, hence each product is adapted for some special field of work.

Internal antisepsis is not attainable, because if the antiseptic were sufficiently powerful to destroy bacteria it must necessarily exhibit a toxic action on the human system. However, in certain lines, this class of antiseptics serve admirably in inhibiting the development of milder types of bacteria and neutralising the action of toxins in infections of the respiratory and urinary tracts. Combinations of bismuth and various antiseptics have become popular in treatment of intestinal disturbances due to fermentative changes or infection.

Inorganic antiseptics. More important and recent are fluorol (sodium fluoride), calcinol (calcium iodate), dymal (didymium salicylate), aluminium fluoride, iodine trichloride and tribromide, magnesium permanganate, vanadic acid, sodium perborate.

Peroxides. The peroxides of the alkaline earths possess antifermentative as well as antiseptic action owing to their generation of hydrogen peroxide and liberation of oxygen when in contact with water. Commercially known are the peroxides of magnesium (D. R. P. 171372), calcium, strontium and zinc (D. R. P. 171372); also sold under copyrighted titles as Gorit (CaO_2), Biogen (MgO_2), Dermogen and Ektogen (ZnO_2).

Colloidal silver is sold as Collargol (Heyden) and Lysargin (Kalle).

Aluminium, organic salts. These combine the astringent properties of aluminium salts with the disinfectant action of the respective organic acids.

Aluminium aceto-tartrate 'Alsol.'	Aethenstaedt.
„ salicylate 'Salumin.'	Riedel.
„ zinc acetate 'Zinol.'	Lewinsohn.
„ boro-formiate.	
„ „ tartrate 'Boral.'	
„ caseinate.	
„ formiate 'Alformin'	Elb.
„ gallate, basic, 'Gallal'	Riedel.
„ β-naphthol disulphonate 'Alumnol'	Hoechst.
„ *p*-phenol sulphonate 'Sozal.'	
„ potassium salicylate 'Alkasal'	Aethenstaedt.
„ sodium acetate 'Acetonal'	Aethenstaedt.
„ sozoiodolate	Trommsdorf.
„ boro-tannate 'Lutol.'	

Bismuth organic salts are of use in gastric or intestinal disturbances, the compounds splitting up into their constituents. Only those sold under registered names are given.

Bismuth albuminate 'Bismutose'	Kalle.
„ bilacto-monotannate 'Lactanin.'	
„ bitannate 'Tannismut'	Heyden.
„ borophenate 'Marcasol.'	
„ chrysophanate 'Dermol.'	
„ cinnamate 'Hetoform'	Kalle.
„ colloidal 'Bismon'	Kalle.
„ dithiosalicylate 'Thioform'	Speyer.
„ gallate 'Dermatol.'	
„ iodo-resorcin-sulphonate 'Anusol'	Schering.
„ „ gallate 'Airol'	La Roche.
„ „ salicylate 'Iodylin.'	
„ „ tannate 'Ibit'	G. C. I. Basel.
„ methylene digallate 'Bismal'	Merck.
„ β-naphthalate 'Orphol.'	Heyden.
„ nosophenate 'Eudoxin'	Rhenania.
„ para-nucleinate 'Parabismut.'	
„ pyrogallate 'Helcosol'	Merck.
„ quinolin-sulphocyanate 'Crurin'	Kalle.
„ tetrabrompyrocatechin 'Noviform'	Heyden.
„ tribromphenate 'Xeroform'	Heyden.

Mercurial antiseptics and mercurials. The value of mercury in treatment of syphilis and also in antiseptics, has brought out a great variety of combinations, some of which, because of their ready solubility, freedom from irritation, and slow elimination from the system, are especially adapted for subcutaneous and intramuscular injection. Others represent antiseptics equal in value to corrosive sublimate yet free from its objectionable action on instruments. With a few exceptions, only such as are marketed under registered names are enumerated. Others are given in Merck's List.

Apallagin. Mercury nosophen (tetra-iodo-phenolphtalein), Hoechst.

Asiphyl. Mercury atoxyl (paranilide arsenate).

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[1] Arch. exp. Pharmakol, 47, 50, Zeitsch. physiol. Chem. 39.

[2] Standardizing of Disinfectants, J. Royal Institute of Public Health, London, 1908; Experimentelle Pharmakologie. H. Meyer and R. Gottlieb, Berlin, 1910; Jour. Hygiene, London, vol. viii., No. 5, Chick and Martin; Jour. Amer. Medical Assoc., vol. lv. p 1635, Post and Nicoll.

Antiperiostin. Mercury iodocantharidate (D. R. P. 163219), A. Klein, Berlin.
Asterol. Mercury *p*-sulphophenate with ammonium tartrate (D. R. P. 104904), La Roche.
Calomelol. Colloidal calomel (U. S. Pat. 740855) Heyden.
Enesol. Mercury salicylo-arsenate, Clin & Co., Paris.
Hermophenyl. Mercury sodium disulphonate, Merck.
Hydrargol. Mercury succinimid, Gehe Co.
Hydrargotin. Mercury tannate, Hell Co.
Hydrargyroseptol. Quinoline mercury-sodium chloride, Fritzsche.
Hyrgol. Colloidal mercury, Heyden.
Lévurargyre. Mercury nucleoproteid, Adrian, Paris.

Mercury phenates. The monophenol derivative, which is quite unstable in the body, is a valuable mercurial, whilst the diphenyl mercury is very poisonous because of its cumulative action. Dimethyl and diethyl mercury are similar. Such organic salts as the benzoate, tribrom-phenol acetate, &c., when used subcutaneously, accumulate locally and frequently produce mercurial poisoning.

Mercury ethyl chloride, albuminate, cacodylate and mercuric chloride-urea are used subcutaneously.

Anogon. Mercury-salt of diiodo-*p*-phenolsulphonic acid (30 p.c. iodine and 50 p.c. mercury), Trommsdorff.
Mercurol. Mercury nucleinate (U. S. Pat. 637355), Parke, Davis.
Mercuriol. Mercury amalgam with aluminium.
Mercochinol. Mercury hydroxyquinoline sulphonate, Fritzsche.
Mergal. Mercury choleate with albumin tannate, Riedel.
Meriodin. Mercury soziodolate (di-iodo-*p*-phenolsulphonate).
Phenegol. Mercury potassium *p*-nitrophenol sulphonate.
Sublamine. Mercuric sulphate ethylenediamine (U. S. Pat. 726125), Schering.

Copper compounds.

Cupratin. Copper albuminate.
Cupriaseptol. Copper *m*-phenolsulphonate, Gawalowski, Berlin.
Cuprol. Copper nucleinate, Parke Davis.

Organic silver antiseptics. Although it is one of the standard remedies for the treatment of infected and inflammatory conditions of mucous surfaces, silver nitrate possesses an irritating and caustic action which greatly restricts its usefulness. Apart from this, it has only a limited penetrating power, due to the fact that it is precipitated by albumin and sodium chloride, ordinary constituents of tissues and their secretions. This is a serious disadvantage, since many of the conditions in which it is employed are due to micro-organisms, which are found not only in the superficial, but also in the deeper portions of the mucous surfaces, and hence cannot be reached by solutions of this chemical, owing to the formation of an insoluble silver albuminate in the upper layers. The recognition of these drawbacks has led to the many new organic compounds of silver now on the market. The older organic salts have been practically superseded by the protein compounds. They are non-irritating when properly employed and are, with few exceptions, unaffected by either albumin or chlorides. They should never be boiled nor mixed with drug extracts.

Albargin. Gelatose silver (15 p.c. silver) (D. R. P. 146792) Hoechst.
Argentamine. Ethylene diamine silver nitrate (10 p.c. silver nitrate) (D. R. P. 74634), Schering.
Argentol. Silver quinaseptolate (31·7 p.c. silver) Fritzsche.
Argonin. Casein silver (4·3 p.c. silver) (U. S. Pat. 575277), Hoechst.
Argyrol. Silver vitellin (20–25 p.c. silver), Barnes.
Hegonon. Ammonio-silver nitrate albumose (7 p.c. Ag) (U. S. Pat. 567412), Schering.
Ichthargan. Silver sulphoichthyolate (30 p.c. silver), Merck.
Nargol. Silver nucleinate (10 p.c. silver), Parke Davis.
Novargan. Silver proteinate (10 p.c. silver) (U. S. Pat. 19989), Heyden.
Omorol. Protein silver (10 p.c. silver), Heyden.
Protargol. Protein silver (8·3 p.c. silver) (U. S. Pat. 615970), Bayer.
Sophol. Methylene nucleinic acid silver compounds (20 p.c. silver) (D. R. P. 852545), Bayer.
Silver salts. Citrate (Itrol, Heyden); electrolytic colloidal silver (Electrargol, Heyden); eosolate (acetyl guaiacol-tri-sulphonate); fluoride (Iachiol); lactate (Actol, Heyden); picronitrate (Picratol, Wyeth); sulphophenate (Silberol). Colloidal silvers are Collargol (Heyden), argoferment (Fritz), and Syrgol (Siegfried).

Inorganic salts of nucleinic acids. Nucleinic acid, a substance common to the blood corpuscles, organs, and vital tissues of the animal organism, has suggested itself as a means for the more ready and effectual administration of metals. The hypothesis that inorganic salts of the heavy metals pass into the blood only so far as they combine with the nucleinic acid, would seem to offer sufficient ground for the artificial preparation of derivatives which would be more readily absorbed and utilised in the human organism. Apart from this, certain of these combinations are especially adapted for external use as antiseptics because of their penetrability, freedom from irritation and decomposition by contact with albuminoids. These combinations comport themselves quite differently from the other more common organic salts, in that the usual inorganic reagents fail to produce any of the characteristic qualitative reactions. For example, copper nucleinate fails to turn blue upon the addition of ammonia water, nor does it react with hydrogen sulphide. The addition of chlorides fails to precipitate silver from these organic combinations.

Nucleinic acid may be obtained from the blood, salmon sperm, and yeast; from the latter source the acid is prepared by extracting with an alkali, when, after acidifying with acetic acid, the albuminoids are coagulated by heating to 75°; from the filtrate the crude nuclein is precipitated by means of acidified alcohol. Purification is effected by careful oxidation with permanganate. The slightly alkaline nuclein solution is then brought into reaction with the salts of silver, mercury, iron, &c., and then precipitated by the addition of alcohol and a neutral salt. In such combinations as the nucleinate or other albumin derivatives of the metals, the latter are retained in the albumin molecule in a masked (larvated) state beyond the reach of the usual inorganic reagents. In the case of the iron preparations we have a ready means of distinguishing this masked metal from that present in the form of the ordinary organic salts, as the peptonate, lactate, &c., in the well-known Macallum's test. This consists in adding a few drops of a 1 p.c. solution of hæmatoxylon to the solution of the preparation, whereby a blue to blue-black coloration ensues if it belongs to the latter class.

Cuprol. Copper nucleinate (6 p.c.), Parke Davis.
Argyrol. Silver vitellin (30 p.c.), Barnes Co.
Ferratogen. Iron nucleinate, Basel, C. F.
Mercurol. Mercury nucleinate (10 p.c.) (U. S. Pat. 637355), Parke Davis.
Nargol. Silver nucleinate (10 p.c.), Parke Davis.

Organic iodine derivatives.—*External iodoform type.* The organic iodine combinations are our standard antiseptics, especially intended for dry local application. Their bactericidal effect depends upon the action of the alkaline wound secretions in splitting up the compounds into their component parts. Iodoform is antiseptic only under conditions in which iodine is slowly eliminated. The newer combinations have aimed at overcoming the objectionable odour and occasional tendency to iodine poisoning peculiar to iodoform, also to combine a lower percentage of iodine with an antiseptic nucleus, securing thereby a milder iodine effect in conjunction with that of the nucleus. Many of this class are of considerable value.

Aristol. Diiodothymol $[C_6H_2(OI)(CH_3)\cdot C_3H_7]_2$ Bayer.
Chrysoform. Dibrom-diiodo-hexamethylenetetramine Merck.
Diiodoform. Ethylene periodide, C_2I_4, Schering.
Europhen. Di*iso*butyl cresol iodide $C_6H_2(C_4H_9)(CH_3)(OI)\cdot C_6H_2(CH_3)(:O)(C_4H_9)$ m.p. 110° (U. S. Pat. 495204), Bayer.
Formidin. Methylene disalicylic iodide $C_{15}H_{10}O_2I_6$ Parke Davis.
Griserin. Isomeride of loretin (D. R. P. 187943) Griserin Werke, Berlin.
Iodanisol. *o*-Iodo-anisol $C_6H_4I\cdot OCH_3$, m.p. 47° Merck.
Iodocrol. Carvacrol iodide $C_{13}H_{13}OI$, Merck.
Iodoformal. Iodoformin ethyl iodide, m.p. 128° (D. R. P. 87812), Marquart.
Iodoformin. Hexamethylenetetramine iodoform $CHI_3(CH_2)_6N_4$ m.p. 178°, Marquart.
Iodoformogen. Iodoform albumin (D. R. P. 95580), Knoll.
Iodogallicin. Bismuth hydroxyiodidemethyl gallol $C_6H_2(OH)_2(COOCH_3)(OBi\cdot I\cdot OH)$ Sandoz.
Iodol. Tetraiodopyrrol C_6I_4NH (D. R. P. 35120), Kalle.
Iodolen. Iodised albumin. Kalle.
Iodolin. Quinoline chloromethyl-iodo-chloride.
Iodophenin. Iodophenacetin, m.p. 130° (D. R. P. 58404), Riedel.
Iodothymoloform. Iodised thymoloform m.p. 150°, Henning.
Iodozol. Sozoiodolic acid (diiodo *p*-phenolsulphonic acid) $C_6H_2I_2(OH)SO_3H+3H_2O$ Trommsdorf.
Iothion. αγ-diiodopropane-β-ol $CH_2I\cdot CH(OH)CH_2I$ Bayer.
Isoform. *p*-Iodoxy anisole $C_6H_4(OCH_3)IO_2$ (D. R. P. 161725), Hoechst.
Loretin. 3-Iodo-4-hydroxyquinoline-1-sulphonic acid (D. R. P. 72924), Schuchardt.
Losophan. Tri-iodo-metacresol $CH_3\cdot C_6HI_3\cdot OH$ m.p. 121°, Bayer
Nosophen. Tetra-iodo-phenolphthalein (D. R. PP. 86069, 143596), Rhenania.
Sanoform. Di-iodo-salicylic methyl ester $C_6H_2(COOCH_3)(OH)I_2$ m.p. 110·5°, Hoechst.
Traumatol. Mono-iodo-cresol, Chevrier and Kraus, Paris.
Vioform. Iodo-chlor-hydroxyquinoline $C_9NH_6(OH)ICl$ (D. R. P. 117767), Basel.

For internal use. These are intended to replace the alkali iodides, claimed to be free from disagreeable taste, digestive disturbances, and tendency to produce iodism.

Iodalbacid. Iodised albumin (10 p.c. iodine), Gans.
Iodalbin. Iodised albumin (21·5 p.c. iodine), Parke Davis.
Iodeigons. An α-iodised albumin (20 p.c. iodine), sodium salt (15 p.c. iodine), Helfenberg.
β-Eigon, an iodised peptone.
Iodglidin. Iodised gluten (10 p.c. iodine), Klopfer.
Iodin. Iodised arachis oil.
Iodipin. Iodised sesamé oil (10 and 25 p.c. iodine) (D. R. P. 96495), Merck.
Iodival. Iodo-mono*iso*-valeryl urea $(CH_3)_2CH\cdot CHI\cdot CO\cdot NH\cdot CO\cdot NH_2$ m.p. 180° (D. R. P. 197648), Knoll.
Iodlecithin, 7 to 8 p.c. iodine (D. R. P. 155629), Riedel.
Iodomenim. Iodised casein containing bismuth (10 p.c. iodine) (D. R. P. 177109), Wuelfing.
Iodothyrin. Lactated active principle of thyroid gland (U. S. Pat. 686648), Bayer.
Iodyloform. Iodised gelatin (10 p.c. iodine), Kohlmeyer.
Sajodin. Mono-iodo-behenate of calcium (5 p.c. iodine) (U. S. Pat. 848230). Iron sajodin contains in addition 5·7 p.c. Fe. Bayer.

Formaldehyde derivatives. Formaldehyde is still sold under registered names such as Formal, Formysol, Holzin, Camolin, Methylal, Steresol. It has virtually supplanted all other embalming fluids. On account of the readiness with which it forms non-irritating condensation-products, the formaldehyde derivatives have been favourably received. These combinations usually form inodorous powders which, when in contact with the alkaline wound secretions, break up with liberation of formaldehyde.

Amyloform. Formaldehyde-starch (D. R. P. 92259), Gans.
Chinoform. Cinchotannicacid-formaldehyde, also quinine formiate.
Chrysoform. Dibrom-monoiodo-hexamethylene tetramine.
Empyroform. Formaldehyde tar condensation product, Schering (U. S. Pat. 761260).
Euguform. Acetylated-methylene guaiacol, Guestrow.
Formaldehyde casein, Merck.
Formicin. Formaldehyde acetamide compound, Kalle.

Forman. Chloromethyl-menthyl ether $C_{10}H_{19}O{\cdot}CH_2Cl$ b.p. 160° (16 mm.) (D. R. P. 119008), Lingner.

Fortoin. Methylene dicotoin (D. R. P. 104362). $CH_2(C_{14}H_{11}O_4)_2$ m.p. 211°–213°, Zimmer.

Glutol. Formaldehyde gelatin (D. R. P. 104365), Schering.

Phenyform. Condensation product of formaldehyde and phenol $[C_6H_4(OH)CH_2OH]_x CH_2O$ Phenyform Co., Berlin.

Tannoform. Methylene ditannin $CH_2(C_{14}H_9O_9)_2$ (D. R. P. 88841), Merck.

Thymoloform. Condensation product of formaldehyde and thymol $(C_6H_3(CH_3)(C_3H_7)O)_2CH_2$ Henning.

Sulphurated products. Salts of sulphonated tars obtained by the destructive distillation of fossilised fish or from petroleum are used as antiseptics. The first of this class to be introduced was:

Ichthyol, the ammonium salt of so-called ichthyol-sulphonic acid obtained by sulphonating the fossilised fish-tar. Other combinations are ichthalbin (ichthyol albumin), ichthargan (ichthyol-silver), ichthermol (ichthyol mercury), ichthoform (ichthyol formaldehyde), ichthyolidin (piperazin ichthyolate), etc. Cordes and Merck.

Products of similar nature are isarol, petrosulfol, sulfogenol, ichthosulfol, ichthynat.

Nafalan, similar to naftalan, Nafalan Co., Magdeburg.

Naftalan. Distillations-residue, free from resin and asphalt, obtained from Caucasian petroleum mixed with sodium stearate, Naftalan Co., Dresden.

Thiol. Sulphurated paraffin oil (D. R. P. 38416), Riedel.

Thiogenol. Sulphonated sulpho-oil, La Roche.

Sulfidol. Colloidal sulphur (D. R. P. 164664), Heyden.

Thilaven. A solution of linalylacet-thiozonide in an alkali thiozonate, 5 p.c. total sulphur, Helfenberg.

ANTISEPTICS CONTAINING PHENOL NUCLEI

During the last few years very few new derivatives of this class have appeared, although much work has been accomplished in tracing the groups to which their destructive action on pathogenic bacteria is due. The caustic action of phenol on the skin and mucus surfaces resides, without doubt, in the hydroxyl group which is also common to its homologues. The local antiseptic properties decrease with an increase in the number of hydroxyl groups as is the case with resorcinol and pyrogallol. Their toxicity increases with the number of hydroxyls. The relative positions occupied by these groups determines likewise relative toxicity, thus the *o*-dihydroxybenzene (pyrocatechol) is the most toxic, while the meta (resorcinol) is the least. The toxicity of phenols diminish, while antiseptic properties increase, by the introduction of alkyl radicles in the nucleus (cresol).

If the hydroxyl groups be closed by etherification, the phenols lose their peculiar caustic and antiseptic action as with veratrole, anisole, and phenetole. That this is not the case with the safroles is due to an active double-linked side chain. In the same way the relative toxicity of the polyhydric phenols is diminished by introduction of acid radicles in place of the hydroxyl hydrogens. Thus, such esters of pyrogallol as eugallol (mono-acetate), lenigallol (tri-acetate) and saligallol (di-salicylate) are comparatively non-toxic owing to their insolubility and the slowness with which they break up when applied to a mucus surface.

If a carboxyl group is introduced into the benzene ring, an acid (benzoic) of low antiseptic power and but slight medicinal activity results, which, however, increases with the molecular weight of the entering acid, as, for example, phenylacetic acid, phenyl propionic acid, and phenyl-butyric acid. On the other hand, the antiseptic powers of the aliphatic acids increase with decreasing molecular weight. Whilst the entrance of chlorine in aliphatic bodies lends hypnotic and narcotic properties, the replacement of hydrogen in the benzene nucleus by a halogen raises the antiseptic properties of the substance. No hypnotic action is discernible, since the human organism is incapable of splitting the halogen off from the nucleus. A comparative study of the relationship between chemical constitution and disinfectant action of antiseptics by Bechhold and Ehrlich (Zeitsch. Physiol. Chem. 1906, 47, 173), has cleared up this subject in a remarkable manner. The experiments were carried out on diphtheria bacilli and other pathogenic bacteria as *B. coli*, pyocyaneus, typhi, &c.

1. The introduction of halogens in phenol raises the disinfectant action corresponding to the number of halogen atoms (1 mol. of penta bromphenol is the equivalent of 500 mol. of phenol).

2. The introduction of alkyl groups in phenol and halogen phenols increases disinfectant action (tribrom-*o*-cresol is 20 times as active as tri-brom-phenol; tetra-brom-*o*-cresol is in effect 250 times as active as phenol and half as toxic).

3. The direct linkage of two phenols or halogen phenols through agency of a CH_2 or $CHOH$ or $CHOCH_3$ or $CHOC_2H_5$ group increases antiseptic action.

4. The union of two phenol groups through CO or SO_2 lessens disinfectant action.

5. The introduction of $COOH$ group into the nucleus lessens disinfectant action.

Among the newer disinfectants of high antiseptic powers against pathogenic bacteria are:

Tetrabrom-*o*-cresol (almost non-toxic) arrests diphtheria bacilli in a dilution of 1 to 200,000 (phenol 1 to 800). In dilution of 1 to 320,000 destroys bacteria in 24 hours.

Tetrabrom-*o*-diphenol (slightly toxic), a dilution of 1 to 640,000 corresponding to 1 to 800 of phenol.

Hexabromodihydroxydiphenylcarbinol (non-toxic) dilutions of 1 to 200,000 corresponding to 1 to 800 of phenol.

The introduction of halogens in phenol depresses at first the toxicity, increasing and reaching a maximum in the penta-halogenphenol. The tri-halogen derivative is equally toxic with phenol.

The introduction of the CH_3 group compensates the toxic action of halogens.

Acetozone. Acetyl benzoyl peroxide $C_6H_5CO{\cdot}O{\cdot}O{\cdot}COCH_3$ m.p. 36·6° (U. S. Pat. 710005), Parke Davis.

Antinosin. Nosophen sodium. *See Nosophen.*

Antisepsin (asepsin) *p*-brom-acetanilide, m.p. 165°, Benzonaphthol. Benzo-β-naphthol $C_6H_5{\cdot}COOC_{10}H_7$ m.p. 110°, Hoechst.

Bromol. Tribromophenol, m.p. 95°, Heyden.

Bromotan. Bromtannin methylene urea, Voswinkel.

Chinosol. Normal hydroxyquinoline sulphate
$(C_9NH_7O)_2H_2SO_4$
m.p. 175°–177·5° (U. S. Pat. 906918), Fritzsche.

Chrysoidin. Diaminoazobenzene hydrochloride
$C_6H_5N:N{\cdot}C_6H_3(NH_2)_2{\cdot}HCl$

Cresol preparations. Because of the insolubility of this antiseptic, different methods of suspending it in water have been resorted to. One class employs fats or resin mixed with pure or crude cresols which are then saponified. Among this class are creolin (Pearson), creosapol (de Haen), creosolin, cyllin (Jeyes Co., London), lysol (Schuelke and Mayer), &c. Another class sulphonate or acetylate cresols as solveol (Heyden), sanatol (Leonhardt), kresulfol (Riedel), kresin (Schering).

Diaphtherin. Hydroxyquinaseptol
$(C_9H_6N{\cdot}OH)_2C_6H_4(OH)SO_3H$
m.p. 85°, Hoechst.

Epicarine. *ω*-Naphthoxy-*o*-hydroxytoluic acid
$CO_2H{\cdot}C_6H_3(OH)CH_2{\cdot}O{\cdot}C_{10}H_7$
(U. S. Pat. 671622) m.p. 190°–195°, Bayer.

Euguform. Acetylated methylene diguaiacol, Hillringhaus.

Europhen. Isobutyl-*o*-cresol iodide
$C_6H_2(C_4H_9)(CH_3)(OI){\cdot}C_6H_2(CH_3)(:O)({\cdot}C_4H_9)$
m.p. 110° (D. R. P. 56830), Bayer.

Euphorin. Phenyl urethane
$CO(NH{\cdot}C_6H_5)(OC_2H_5)$ m.p. 50°, Heyden.

Hetocresol. *m*-Cresol cinnamate
m.p. 65° (D. R. P. 99567), Kalle.

Lygosins. Sodium and quinine salts of dioxydibenzalacetone
$CO:(CH:CH{\cdot}C_6H_4{\cdot}ONa)_2+7H_2O$
(D. R. P. 110521), Zimmer.

Nizin. Zinc sulphanilate, Burroughs.

Nosophen. Tetra-iodo-phenolphthalein
(D. R. P. 143596), Rhenania.

Paralysol. Solid cresol combination
$C_6H_4(CH_3)OK{\cdot}3C_6H_4(CH_3){\cdot}OH$ m.p. 146°.

Of value in granulative processes is amino-azo-toluene rendered not toxic by acetylation of its amino group, and called *azovernin*, m.p. 185° (A. G. f. A.). *Pellidol*, colourless diacetyl amino-azo-toluene (A. G. f. A.) is an improvement on Scarlet R (amino-azo-toluene coupled with *β*-naphthol).

Antiseptics, internal. This class is chiefly employed in diseases of the air passages. Apart from their antiseptic properties, the phenols possess more or less of an analgesic and local anæsthetic effect which, however, cannot be utilised unless substitution be resorted to in order to eliminate the caustic effect of the hydroxyl already referred to. Guaiacol
$(C_6H_4(OH)OCH_3(1:2)$
possesses in general an action similar to phenol and pyrocatechol, but is less toxic and caustic and has greater antipyretic effect. Because of its disagreeable taste and more irritant action upon the stomach compared with guaiacol, creosote has been largely replaced by the former. Guaiacol and its preparations excite the nervous centres, stimulating thereby the assimilative processes, also the activity of the leucocytes, elimination of the bronchial secretions and kidneys. The undesirable caustic and secondary effects of guaiacol and creosote formerly militated against their more general use until the influence of substituting groups was better understood. As has been pointed out, the toxicity of the dihydroxybenzenes depend on the presence of the free OH groups, reaching a maximum convulsive effect in pyrocatechol. If both hydroxyls are methylated, the product (veratrole) becomes three times less toxic than guaiacol, with, however, a disappearance of medicinal action. One hydroxyl must remain free or loosely covered if we desire to retain the specific properties of guaiacol. One method of accomplishing this is shown in the carbonic acid esters as duotal or creosotal, which are tasteless and non-irritant. The easily hydrolisable organic acid esters as benzosol, styracol, &c., are perhaps more readily absorbed in the intestinal canal. Another class of derivatives with a free hydroxyl group in which the nucleus is substituted are the ortho-guaiacol sulphonic acid (thiocol), the para derivative (monotal) possesses an undesirable action on the stomach. Condensation-products with formaldehyde in which two guaiacol radicles are linked by means of a methylene group (pneumin, euguform, pulmoform) liberate formaldehyde in minute traces. These products are quite insoluble, breaking up very slowly. Substitution in the nucleus, while yielding more soluble compounds, diminishes medicinal activity.

Aethacol (thanatol). Pyrocatechin monomethyl ether b.p. 210°, Kalle.

Benzosol. Guaiacol benzoate
$C_6H_5{\cdot}COO{\cdot}C_6H_4{\cdot}OCH_3$
m.p. 60° (U. S. Pat. 453035), Hoechst.

Cacodyliacol. Guaiacol cacodylate
$C_6H_4(OCH_3){\cdot}As(CH_3)_2O_2$ Merck.

Creosotal. Creosote carbonate (U. S. Pat. Exp. 501235), Bayer, Heyden.

Eucol. Guaiacol acetate
$C_6H_4(OCH_3)O{\cdot}COCH_3$
b.p. 235°–240°, C. Erba, Milan.

Euguform. Acetylated condensation product of guaiacol and formaldehyde, Hillringhaus.

Eosote. Creosote valerate, b.p. 81°–85° (3 mm.), Lehmann.

Duotal. Guaiacol carbonate (U. S. Pat. 466913), Bayer.

Geosote. Guaiacol valerate
$C_6H_4(OCH_3)O{\cdot}CO{\cdot}C_4H_9$ b.p. 260°, Lehmann.

Guaiacetin. Pyrocatechin sodium acetate
$C_6H_4(OH)OCH_2{\cdot}COONa$
m.p. 130°, Van Gember.

Guacamphol. Guaiacol camphoric ester
$C_8H_{14}(COO{\cdot}C_6H_4{\cdot}OCH_3)_2$
m.p. 126°, Henning.

Guaiachinol. Quinine dibromoguaiacolate
$C_6H_2Br_2(OCH_3)OH{\cdot}Q$

Guaiaperol. Guaiacol-piperidine
$C_5H_{11}NH{\cdot}C_6H_4(OH)OCH_3$ m.p. 80°.

Guaiacyl. Calcium orthoguaiacol sulphonate (local anæsthetic)
$(C_6H_3(OH)(OCH_3)SO_3)_2Ca$

Guaiaform, Geoform. Condensation product of guaiacol and formaldehyde, Henning.

Guaiamar. Glycerol guaiacolate
$C_6H_4(OCH_3){\cdot}O(CH_2OH{\cdot}CHOH{\cdot}CH_2)1:2$
m.p. 75° (U. S. Pat. 599125), Mkd't.

Guaiasanol. Diethyl glycocoll guaiacol HCl.
$C_6H_4(OCH_3){\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}N(C_2H_5)_2{\cdot}HCl$
m.p. 183° (U. S. Pat. 624772), Hoechst.

Guatannin. Guaiacol-tanno-cinnamate (D. R. P. 133299), Berlin Lab.

Kreosal. Creosote tannate.

Monotal. Guaiacol methyl glycolate $CH_2(O{\cdot}CH_3)COO(C_6H_4{\cdot}OCH_3)$ b.p. 156° (15 mm.) (U. S. Pat. 822339), Bayer.

Pneumin. Methylene creosote (cond.-prod. formaldehyde and creosote), Speier.

Phosote. Creosote phosphate, b.p. 190°–203°.

Pulmoform. Methylene guaiacol. *See Pneumin.* Speier.

Salocreol. Creosote salicylate, Heyden.

Styracol. Guaiacol cinnamate, m.p. 130° (D. R. P. 62176), Knoll.

Tanno-cresoform and guaiaform. Comp. of creosote or guaiacol with tannin by aid of formaldehyde.

Taphosote. Tannophosphate of creosote, Lambiotte Fr., Paris.

Thiocol. Guaiacol sulphonate of potassium $C_6H_3(OH)(OCH_3)(SO_3K)$, 1 : 2 : 6 (U. S. Pat. 650218), La Roche.

Intestinal antiseptics. These compounds are intended to break up only under the influence of the alkaline intestinal secretions. Intestinal asepsis is unattainable, nevertheless numerous combinations serve valuable purposes in securing partial disinfection, inhibiting the development of milder types of bacteria, neutralising the action of toxins and arresting disturbing fermentative action in the canal. The many organic bismuth compounds serve in this capacity (as marcasol, thioform, iodylin, &c.), also various phenol esters of salicylic acid as salol, also guaiacol esters, naphthyl esters (alphol and betol).

Alphol. α-Naphthyl salicylate, m.p. 83°.

Benzonaphthol. β-naphthyl benzoate, m.p. 110°, Hoechst.

Betol. β-Naphthyl salicylate, m.p. 95°.

Chinaphthol. β-Naphthyl monosulphonate of quinine, m.p. 185°, Merck.

Enterol. Tricresol (pure cresol), Schering.

Eugenoform. Eugenolcarbinolsodium, m.p. 160°.

Isoform. *p*-Iodoxyanisole $C_6H_4{\cdot}OCH_3{\cdot}IO_2$ (D. R. P. 161725), Hoechst.

Kresalol. *m*-Cresol salicylate $CH_3{\cdot}C_6H_4{\cdot}O{\cdot}OC{\cdot}C_6H_4{\cdot}OH$ m.p. 74°.

Salacetol. Acetol-salicylic acid $C_6H_4(OH)COO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$ m.p. 71°, Schoetensack.

Salithymol. Salicylic thymyl ester $CH_3{\cdot}C_6H_3(C_3H_7)O{\cdot}COC_6H_4(OH)$

Lactol. β-Naphthyl lactate $CH_3{\cdot}CH(OH)COO{\cdot}C_{10}H_7$

Intestinal astringents. These consist chiefly of condensation-products or similar compounds of tannin with formaldehyde or hexamethylene tetramine. In order to secure their astringent and other medicinal effects upon the intestinal mucus surface for relieving inflammatory conditions and retarding bacterial action, such combinations are intended to pass through the stomach unchanged and break up into their constituent parts under the influence of the alkaline secretions. They are chiefly employed in catarrhal and inflammatory conditions as dysentery, tubercular diarrhœa, cholera, &c.

Gallogen. Egallic acid (D. R. P. 137033–4), Heinemann.

Honthin. Keratinised tannin albuminate, Hell Co.

Rexotan. Methylene tannin urea, Voswinkel.

Tanargan. Tannin silver albuminate, Weil.

Tannalbin. Tannin albuminate (U. S. Pat. 563479), Knoll.

Tannigen. Diacetyl tannin (U. S. Pat. 533718), Bayer.

Tannisol. Methylene ditannin, Wôlfrum.

Tannocasum. Casein tannate.

Tannoform. Methylene ditannin, m.p. 230° $CH_2(C_{14}H_9O_9)_2$ (D. R. P. 88841), Merck.

Tannopin (tannon). Hexamethylenetetramine tannin $(CH_2)_6N_4(C_{14}H_{10}O_9)_3$ (U. S. Pat. 607172), Bayer.

Tannothymal. Condensation product of formaldehyde, thymol and tannin (D. R. P. 188318), Schimmel Co.

Tannyl. Tannin oxychlor casein, Gehe Co.

Tanocol. Tannin gelatin comp., A. G. f. A.

URINARY DISINFECTANTS.

The representative of this class, urotropin (hexamethylenetetramine), of which there are a number of combinations, breaks up in the system with liberation of nascent formaldehyde, which serves to prevent the development of the more sensitive micro-organisms as staphylococci, coli and typhus bacilli, &c. This class is usually employed in infections of the urinary passages; they also serve as prophylactics against infection in operations involving the bladder.

Amphotropin. Hexamethylenetetramine camphorate $C_8H_{14}{\cdot}(COOH)_2[(CH_2)_6N_4]_2$ Hoechst.

Atophan. Phenyl-quinoline-carbonic acid $C_9H_5N(C_6H_5)COOH$ (2 : 4) m.p. 208°–209°, Schering.

Borovertin. Hexamethylene tetramine triborate $(CH_2)_6N_4{\cdot}3HBO_2$ (D. R. P. 188815), A. G. f. A.

Cystopurin. Double salt of one mol. urotropin and two of sodium acetate, Wuelfing.

Diaphthol (chinaseptol). *o*-Hydroxyquinoline-*m*-sulphonic acid $C_9H_5N(OH)SO_3H$ m.p. 295°.

Galloformin. Comp. of urotropin and gallic acid $C_6H_2(OH)_3{\cdot}COOH[(CH_2)_6N_4]$ Henning.

Helmitol (urapurgol). Anhydro-methylene citrate of urotropin $C_7H_8O_7[(CH_2)_6N_4]$ (U. S. Pat. 722275) m.p. 165°–175°, Bayer.

Hetralin. Resorcinol urotropin $C_6H_6O_2[(CH_2)_6N_4]$

Hexal. Hexamethylenetetramine salicylsulphonic acid $[(CH_2)_6N_4]C_6H_3(OH)(COOH)HSO_3$ Riedel.

Saliformin. Urotropin salicylate Merck.

Urotropin. Hexamethylenetetramine $(CH_2)_2N_4$ m.p. 165°–175°, Schering.

This compound is supplied by other firms under such titles as formin, aminoform, cystamin, cystogen, uritone, &c.

DIATHETICS.

These remedies are employed more especially in uric acid diathesis and also exert an action similar to the previous class. The chief objects sought are either to diminish the production of uric acid or through profuse diuresis, secure thorough flushing, and the elimination of the urates; or by the aid of organic bases bring about solution of the acid urates. The theory of the solubility of the urates in alkaline solutions is based on the experience gained through the use of the salts of the vegetable acids, more especially citric acid, which also possesses a diuretic action. These acids diminish, in addition, the quantity of uric acid secreted. Experimentally, it has been shown that while the acid sodium urate is soluble 1 in 1150 of water, the piperazine salt is soluble 1 in 50 and the lysidin salt 1 in 6. While doubts have been expressed as to the accuracy of some of these theories, the clinical experiments have been generally successful.

Acitrin. 2-Phenylquinoline-4-carboxylic ethyl ester $C_9NH_5(C_6H_5)COOC_2H_5$ m.p. 61°, Bayer.

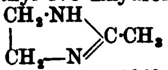
Chinotropin. Urotropin quinate, Schering.

Citarin. Sodium anhydro-methylene citrate $(CH_2COONa)_2:C:(O{\cdot}CH_2{\cdot}O{\cdot}CO)$ (D. R. PP. 129255, 150949), Bayer.

Formurol. Hexamethylenetetramine sodium citrate $C_6H_7O_7Na,C_7H_{12}N_4$, Falkenberg.

Lycetol. Dimethyl piperazine tartrate, m.p. 250° (U. S. Pat. 523018), Bayer.

Lysidin. 2-methyl-4:5-dihydroiminazole



m.p. 106°–105°, Hoechst.

New Sidonal. A mixture of quinic anhydride and quinic acid. Charlottenburg.

New Urotropin. *See Hedonal.* Schering.

Piperazine. Diethylene diamine $NH[CH_2{-}CH_2]_2NH+6H_2O$ m.p. 104° (U. S. Pat. 543214), Bayer, Schering.

Sidonal. Piperazine quinate, m.p. 168°–171° (Eng. Pat. 11420), Charlottenburg.

Solurol. Nucleotin phosphoric acid, Elb.

Urol. Urea quinate, m.p. 106° (D. R. P. 124426), Schulz.

Ursal. Urea salicylate. Erdmann.

The purine derivatives (diuretics). Qualitatively, the diuretic action of the methylated purine derivatives correspond to their influence upon the muscular system, while the reverse is noted in their exciting action on the central nervous system. That is, the stronger the effect of a purine derivative upon the muscular system, the more marked is its diuretic action and the less its influence upon the nervous system. The effect of theobromine on the nervous system is far weaker than that of caffeine, while its diuretic action is equally strong. The relative diuretic action of this class of derivatives depends upon the positions methylated, thus the positions 1 : 3 (theophyllin) and 1 : 7 (paraxanthine) are of greater pharmacological importance than 3 : 7 (theobromine). Trimethylxanthine (caffeine), while possessing a slight diuretic action, exerts a too powerful influence upon the brain for diuretic purposes (Archiv. Exp. Path. u. Phamakologie, 1900, 319.)

The introduction of ethyl groups in place of methyl, produces no material change in action. The objectionable slow action of the methylated xanthines, due to their insolubility, is relieved by combination with organic salts of the alkalis (sodium salicylate, benzoate, acetate) in the form of double salts.

Caffeine derivatives. *Symphorol.* Various alkali salts of caffeine sulphonic acid. With the introduction of sulphonic acid, caffeine loses its effect on the vasomotoric centre, while its diuretic action is retained.

Hetol: Caffeine sodium cinnamate (Kalle).

Dimethyl Xanthines. Theobromine (santheose), 3 : 7 dimethylxanthine.

Agurin.	Theobromine	sodium-sodium acetate. Bayer.
Barutin	,,	barium-sodium salicylate, A. G. f. A.
Diuretin	,,	sodium salicylate, Knoll.
Theobromose	,,	lithium.
Theophorin	,,	sodium-sodium formate, La Roche.
Theolactin	,,	,, ,, lactate, Zimmer.
Urocitral	,,	,, ,, citrate, Rump.
Uropherin	,,	lithium benzoate salicylate, Merck.

Theophyllin (theocin) synethetic 1 : 3-dimethylxanthine, m.p. 268° (D. R. P. 138444), Bayer, Boehringer.

Theocin sodium acetate $C_7H_7N_4O_2Na{\cdot}CH_3COONa+H_2O$ Bayer.

Euphyllin. Theocin ethylene diamine, Byk.

YEAST PREPARATIONS.

These were first introduced into medicine by T. Landau (Deuts. med. Wochschr. 1899, No. 11), and were recommended in treatment of chronic leucorrhœa and especially gonorrhœal affections. Internally, yeast is employed in eczema, anthrax, carbuncles, skin diseases of gastric origin, diabetes and infectious diseases (scarlet fever, erysipelas, measles, &c.). The yeast cells retain their activities in the digestive tract and serve to retard or destroy the toxicity of various pathogenic bacteria.

Cerolin. A solid extract of yeast, containing fat, Boehringer.

Furonculine.	A dry extract of yeast,	La Zyma.
Levuretin.	Dried yeast cells,	Feigel.
Levurinose	,,	Blaes.
Trygase	,,	Riedel.
Zymin	,,	Schroder.
Cerevisine	,,	Grimault, Paris.

ANÆSTHETICS.

We distinguish between products that produce (1) total anæsthesia and (2) local anæsthesia.

Total anæsthetics (by inhalation). This class belongs exclusively to the aliphatic series and depends largely, for its action, upon the presence of chlorine, intensity in action increasing with the number of chlorine atoms introduced; thus CH_3Cl is feebly narcotic, while CCl_4 paralyses the heart. The corresponding bromine derivatives also possess a narcotic effect, but because of their intense action only the ethyl bromide and bromoform are employed, and these internally. Such members of the alkyl halides as have a very low boiling-point, are employed as local anæsthetics by freezing. No improvement over chloroform or ether has appeared, although some of this group serve in certain specific cases (*see* introduction *Hydrocarbons*). More prominent are:

Ethyl chloride C_2H_5Cl, b.p. −29°. Used as inhalant and also as a local anæsthetic.

Ethyl iodide C_2H_5I, b.p. 70°–75°. Inhaled for asthma.

Ethyl bromide C_2H_5Br, b.p. 38°–40°. Total anæsthetic, rapid and short duration.

Ethylene chloride $C_2H_4Cl_2$, b.p. 83°. Inhalant and local anæsthetic.

Ethylene bromide $C_2H_4Br_2$, b.p. 130°. Internally in epilepsy.

Ethylidene chloride $CH_3{\cdot}CHCl_2$, b.p. 58°–60°. Anæsthetic.

Methyl chloride CH_3Cl, b.p. −22°. Local anæsthetic.

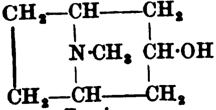
Methylene chloride CH_2Cl_2, b.p. 42°. Inhalant and local anæsthetic.

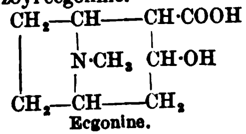
Somnoform. A mixture of ethyl chloride 60 parts, methyl chloride 35 parts, and ethyl bromide 5 parts. Anæsthetic.

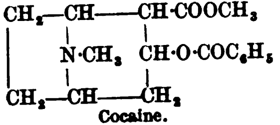
Pental, tri-methyl-ethylene $(CH_3)_2C{\cdot}CH{\cdot}CH_3$, b.p. 38°. Dental anæsthetic.

Local anæsthetics. Cocaine, introduced as local anæsthetic in 1885 by Koller, still retains its popularity because of its intensity and depth of action. Objectionable features are its irritant effects and dilation of the pupil in eye practice, hydrolysis through sterilisation, and excitation and paralysis of the central nervous system. Attempts have been made to find a substance possessing the virtues of cocaine but free as possible from untoward secondary effects. Partial success has been attained, all the compounds are designated stable to sterilisation, and in general, each is specially adopted for certain lines of local anæsthesia.

Modern developments in local anæsthetics are due to studies on the constitution [1] of cocaine, which may be concisely stated as follows: Cocaine is a heterocyclic body with a reduced pyridine ring; this nucleus is called ecgonine, and is the carboxyl derivative of tropine (the base of atropine). Important for the development of local anæsthetic action are the carboxyl group, present as methyl ester and a hydroxyl group, the hydrogen of which is replaced by a benzoyl group. Cocaine is then the methyl ester of benzoyl ecgonine.


Tropine.


Ecgonine.

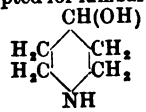

Cocaine.

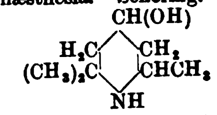
The nuclei tropine and ecgonine are practically devoid of anæsthetic effect. This action also disappears with the removal of either the benzoyl or methyl group from cocaine. The replacement of methyl by other alkyls yields homologues which differ but slightly quantitatively. If other aromatic acid radicles replace the benzoyl group, anæsthetic action is materially lessened or disappears.

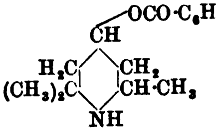
The general conclusions drawn from this are:—that the action of cocaine is dependent upon the presence of a nitrogenated nucleus, an esterified alkyl (COOR), and a benzoyl group; [2] consequently attempts to locate an 'anæsthiophore' nucleus have been without success. [3]

On these assumptions the search for ideal local anæsthetics has progressed in two directions; namely derivatives containing a cyclic nitrogen and the amino and oxyamino benzoic alkyl esters. Closely related to the ecgonine nucleus and containing the piperidine ring of cocaine are the acetonamine derivatives, most important among which is:

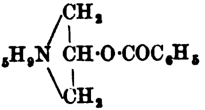
Beta eucaine, used chiefly in the form of lactate (m.p. 152°) or hydrochloride (m.p. 268°) in 2 to 3 p.c. solutions (D. R. P. 97672). Not adapted for lumbar anæsthesia. Schering.


γ-Hydroxypiperidine.


Vinyl diacetone alkamine.

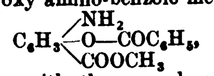

Eucaine B, benzoyl-vinyl-diacetone-alkamine.

Tropa cocaine. The hydrochloride of benzoyl derivative of pseudo-tropine, a *cis*-isomeride of tropine, found in the Japanese coca leaf also prepared synthetically. [1] Used like cocaine and is only ½ to ¼ as toxic; m.p. 271° (U. S. Pat. 628293), E. Merck.



Attempts involving the utilisation of the pyrrol ring of the ecgonine molecule were next made, but these were soon confined to benzene derivatives, since a number of well-known bodies, as creosote, eugenol, &c., belonging to this nucleus, possessed local anæsthetic properties.

Selecting a compound of a constitution analogous to that of cocaine, containing nitrogen, a benzoyl and an esterified alkyl group, namely benzoyl-hydroxy amino-benzoic methyl ester



$$C_6H_3\begin{cases}NH_2\\ O{-}COC_6H_5,\\ COOCH_3\end{cases}$$

in accordance with theory, a local anæsthetic was produced. Subsequent experiments demonstrated that the benzoyl group was superfluous, since a benzene ring was already present, also the benzoyl free compound possessed a more marked anæsthetic action. The phenol hydroxyl was found not to be absolutely essential, although its presence bestowed antiseptic properties.

These experiments, made in 1897 by Einhorn and Heinz, [2] demonstrated that the *esters of aromatic, amino and hydroxyamino acids* possessed, in general, local anæsthetic properties.

The first of this group to be introduced was:

Orthoform, methyl *p*-amino-*m*-hydroxybenzoate, m.p. 120°–121°. A cheaper isomeride followed in—

Orthoform, new methyl *m*-amino-*p*-hydroxybenzoate, $C_6H_3(COOCH_3)(NH_2)(OH)1:2:4$,

---

[1] C. A. Einhorn, Annalen, 311, 26, 254; 325, 305; 359, 145; 371, 125. Jowett, Chem. Soc. Trans. 89, 357; 91, 92; 95, 1020; Pyman, *ibid*. 93, 1793. Willstätter, Ber. 33, 1710; Barrowcliff, Chem. Soc. Trans. 95, 1966.

[2] References to the mydriatic action of cocaine are made under the mydriatics.

[3] Modern Intro-chemistry, Keane, J. Soc Chem. Ind. 1910, p. 391: Physical Chemistry in Service of Medicine, W. Pauli, Fisher.

[1] Ber. Wilstaetter, 33, 1710; Annalen, 317; Pharm. Zeit. 1891, 149; Brit. Mid. J. 1890, 402.

[2] Virchow's Archiv. 1896, 145, 78; 1897, 149, 217 1898, 154, 547

m.p. 142°. Because of their insolubility, these are used dry. The acid soluble salts are irritating and frequently produce necrosis. (U. S. Pats. 610348, 625158.) Hoechst.

Simple alterations in the above formulæ produced—

Anæsthesin, *p*-amino-benzoic-ethyl ester

$C_6H_4(NH_2)(COOC_2H_5)1:4$,

m.p. 90°–91° (D. R. P. 19416 K.). Used locally, especially internally in hyperæsthesia of stomach, gastralgia, excessive vomiting, &c. No secondary effects as yet observed. The hydrochloride of anæsthesin is used hypodermically in 1 to 4 p.c. solutions. Hoechst.

Cycloform, *p*-amino-benzoic-*iso*-butyl ester

$C_6H_4(NH_2)COOC_4H_7$

m.p. 65°. (U. S. Pat. 958110.) Bayer.

Propæsin, *p*-amino-benzoic propyl ester

$C_6H_4(NH_2)(COOC_3H_7)1:4$,

m.p. 73°. Like anæsthesin, it is non-irritant and non-toxic for internal and local uses. (U. S. Pat. 950926.) Fritzsche.

Subcutin (soluble anæsthesin) anæsthesin phenolsulphonate

$C_6H_4(COOC_2H_5)(NH_2{\cdot}SO_3H{\cdot}C_6H_4OH)1:4$

m.p. 195·6°. Ritsert.

In the endeavour to produce a substance related to orthoform, soluble in water with neutral reaction and adapted for subcutaneous use, the following resulted:—

Nirvanin, diethyl-glycocoll-*p*-amino-salicylic methyl ester

$C_6H_3(NHCOCH_2{\cdot}N(C_2H_5)_2)(OH)(COOCH_3)$

m.p. 185°. Used chiefly in dental and eye practice; less toxic but less penetrating than cocaine. Hoechst.

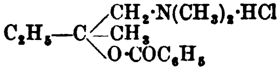
Novocaine, *α*-*p*-aminobenzoyl-*β*-diethylamino-ethane (U. S. Pat. 812554)

$C_6H_4(NH_2)COO{\cdot}CH_2{\cdot}CH_2N(C_2H_5)_2{\cdot}HCl$,

m.p. 156°. This is a diethylamino derivative of anæsthesin, m.p. 155°. Used in conjunction with adrenaline, toxic effects only noticed in lumbar anæsthesia. Claimed to be ⅙ as toxic as cocaine. Hoechst.

In some of the more recent introductions, the amino group has been transferred to the side chain, yielding compounds which represent substituted tertiary alcohols. The dimethylamino groups have a very important bearing on the physiological action of these compounds.

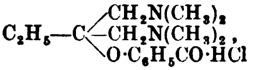
Stovaine, *β*-benzoxy-*β*-methyl-*α*-dimethylaminobutane hydrochloride



$$C_2H_5{-}C\left\langle\begin{array}{l}CH_2{\cdot}N(CH_3)_2{\cdot}HCl\\CH_3\\O{\cdot}COC_6H_5\end{array}\right.$$

m.p. 175°: should not be sterilised above 115°. About ⅓ as toxic as cocaine, used in ½ to 1 p.c. solutions as general all-round local anæsthetic, but especially in spinal anæsthesia. (U. S. Pat. 829374.) Poulenc Frères & Co..

Alypin, hydrochloride of benzoyl *αβ*-tetramethyldiamino-*β*-ethyl-*iso*propyl alcohol



$$C_2H_5{-}C\left\langle\begin{array}{l}CH_2N(CH_3)_2\\CH_2N(CH_3)_2,\\O{\cdot}C_6H_5CO{\cdot}HCl\end{array}\right.$$

m.p. 169°; sterilisable. Used in spinal anæsthesia, also as a non-toxic general local anæsthetic like cocaine. Does not produce mydriasis. (U. S. Pat. 808748.) Bayer.

A slight local anæsthesia was noticed while experimenting with the aniline antipyretics, formanilide being stronger than acetanilide. By the addition of a second basic group to phenetidin derivatives, marked anæsthetic action is developed. To this class belong:

Holocaine, *p*-diethoxy-diphenyl-ethenyl-amidine

$CH_3{\cdot}C:(N{\cdot}C_6H_4OC_2H_5)(NH{\cdot}C_6H_4OC_2H_5){\cdot}HCl$,

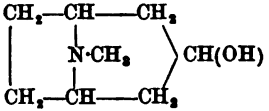
m.p. 189°. Used only in eye practice. Too toxic for subcutaneous use (D. R. P. 80568). Hoechst.

Acoin, di-para-anisyl-monophenetyl-guanidine $C:(N{\cdot}C_6H_4{\cdot}OC_2H_5)(NH{\cdot}C_6H_4{\cdot}OCH_3)_2HCl$, m.p. 176°. Used in eye practice and dentistry. Strong solutions cause irritation. No toxic effects from weaker solutions: less toxic than cocaine. V. Heyden.

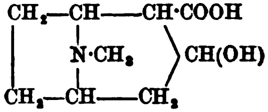
Chloretone, acetone chloroform, trichlorbutyl alcohol $CCl_3(CH_3)_2C{\cdot}OH+\frac{1}{2}H_2O$, m.p. 96°–97°. The 1 p.c. aqueous solution sold under name of anesin (aneson). Employed as local anæsthetic in conjunction with cocaine and adrenaline. Parke Davis.

Adrenaline, anterenol and homorenon, *see* under *Organo-therapeutic agents*.

Mydriatics. Closely related chemically and in some respects pharmacologically are atropine and cocaine. They are derived from a condensation-product of a pyrrolidine and piperidine rings in which the nitrogen and its two neighbouring carbons are common to both. Atropine is a derivative of tropine, an alcohol of such a bi-cyclic nucleus with a methylated nitrogen (I.). Cocaine, a derivative of ecgonine, is an ortho carboxylate of tropine (II.).



I.

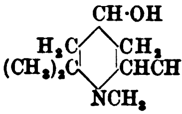


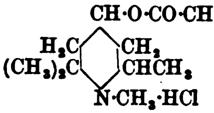
II.

In both, the hydroxyl group is esterified by an aromatic acid, tropic acid

$(C_6H_5{\cdot}CH(CH_2OH)COOH)$

serving in atropine and benzoic acid in cocaine, in addition to the methyl group attached to the carboxyl. Both atropine and cocaine influence alike the central nervous system, first as excitants, then paralysing; they also exert a paralysing influence on the peripheral terminals of certain nerves, whilst cocaine exerts this effect particularly on the sensory nerve terminals, the action of atropine is manifold in other directions. Mydriatically, both alkaloids are alike; cocaine, while producing a less marked dilation of the pupil, has a more prolonged effect. The basic nuclei of these alkaloids occasion a paralysing effect upon peripheral nerve terminals, reaching full development only through substitution. Tropine is not mydriatic, while its action on the heart is influenced by esterification by means of aromatic acids; this latter effect diminishes and that on the nerve terminals is developed, according to the nature of the acid radicle introduced. The tropines of benzoic, cinnamic and salicylic acids possess varying anæsthetic action with but little or no mydriasis. If the esterifying aromatic acid contains an hydroxyl in the side chain, the characteristic mydriatic effect is developed as seen in mandelate of tropine (homatropine). The introduction of other negative radicles in the alcoholic hydroxyl group of the tropic acid radicle does not seem to produce any effect on its activity. By addition of halogenated alkyls, atropine becomes a salt of the quarternary bases, namely alkyl atropinimines, which possess a more evanescent mydriatic and lesser toxic action, such as eumydrin. Of interest in this same series is the use of the unsymmetrical cyclic bases of the acetone alkamine series, for example, in the labile forms of the unsymmetrical (*n*) alkylated bases of the tri-acetone-alkamines, the hydrogen of the hydroxyl, when replaced by the benzoic, mandelic, tropic or phenyl acetic acid radicles, yields mydriatic bodies. If a mandelic acid radicle is introduced in methyl-vinyl-diacetone-alkamine (I.), the mydriatic euphthalmine (II.) results. It is a hydrochloride of (*n*)methyl vinyl-diacetone-alkamine-phenyl-glycol or the hydrochloride of the mandelic acid derivative of eucaine 'B.'


I.


II.

Of simpler constitution and belonging to the pyrrolidine derivatives is the mydriatic mydrol.

Eumydrin. Methylatropine nitrate
$C_6H_5(HO{\cdot}CH_2)CH{\cdot}CO_2{\cdot}C_7H_{11}N(CH_3)_2NO_3$
m.p. 163° (D. R. P. 137662, 138443), Bayer.

Euphthalmine. 1 : 2 : 6 : 6-tetramethyl-4-mandeloxy-piperidine-hydrochloride
(U. S. Pat. 663754), Schering.

Mydrol. Iodomethyl phenyl pyrazolone, m.p. 178°, Merck.

ORGANIC ARSENICALS AND CHEMOTHERAPEUTICS (PARASITOTROPICS).[1]

Whilst many microbial infectious diseases are amenable to serum treatment, there are a number, especially those of protozoal origin, which can only be treated by means of chemical specifics. These react with such micro-organisms in a manner somewhat analogous to that of sera. Study in this direction has been greatly stimulated by the discovery of the protozoal parasites (trypanosoma) of the African sleeping sickness. Through the investigations of Ehrlich and others, considerable attention has been directed to the chemo-therapeutics of spirochetal diseases (syphilitic, intermittent), and those of a malignant parasitic origin, namely the protozoal parasites of the trypanosoma, of which there are several varieties. Parasito-chemicals tend to destroy parasites in the living organism without injury to the tissues or organs, contrary to the organotropic. Ehrlich states that all parasitotropic bodies are also poisonous to the living organism (organotropic), hence such as are curative must contain organo and parasitotropic properties in proper proportions. Such coal-tar colours as are of value in trypanosomiasis may be divided into (*a*) certain azo-dyes, (*b*) certain basic triphenyl methane dyes as *p*-fuchsine, methyl violet, pyronine, &c. To these may be added the organic arsenicals. Ehrlich found that methylene blue was more strongly 'organotropic' than 'parasitotropic,' a dilution of 1 in six million caused cessation of movement *in vitro* when tested on the spirilla of relapsing fever, but with animal experiments it required 500 times as much of the dye. He then tried trypan red (diamino-naphthalene disulphonic acid 2,7,3,6), which was found to possess curative effects in trypanosoma of a certain type (*mal de caderas*); frequently, however, the disease reappeared after intervals. This same effect was peculiar to the azo- colours of the benzidine type. After testing a large number of colours, Ehrlich established the fact that effective bodies must be the tetrazo colours derived from naphthalene disulphonic acids with the sulphonic groups in positions 3 and 6. They must be naphthalene derivatives containing at least one amino and two sulphonic groups. Among the diamines, the di-chlor products were the best, especially those in which the benzene groups are connected by a divalent group (=NH, =CO). The symmetrical colours were found to be less injurious to animals. Malachite and brilliant greens with their di- and tri-hydroxy-derivatives as well as *o*-hydroxyhexamethyl rosaniline exerted curative effects. According to Ehrlich, the toxicity of malachite green is due to its four methyl groups and that of brilliant green to its four ethyl, which is overcome through the introduction of a faintly acid hydroxyl group. He therefore prepared di- and tri-hydroxy- malachite greens which, when combined with trypan red, showed excellent curative effects in nagana infection. Of all the rosaniline derivatives, pararosaniline gave the best results. Most effective was the simultaneous treatment with atoxyl and trypan red or blue or fuchsine.

In conjunction with his study of the colours in treating trypanosoma infection, Ehrlich took up the organic arsenicals in combating spirochetal diseases, more especially syphilis. After the elucidation of the constitution of atoxyl, a great variety of other arsenical organic derivatives were synthesised and studied pharmacologically, finally resulting in the discovery of the Ehrlich-Hata '606.' The arsenical preparations have always been employed in diseases arising from disturbances of the nutrition or of malarial origin, and through recent researches in syphilis, diseases of syphilitic and protozoal origin. Some years ago it was discovered that cacodylic acid and its salts, because of their stability, suffered but little change in the organism, 1 grm. of the sodium salt (containing ½ as much As_2O_3 as arsenic acid) could be taken without harm. Inorganic arsenic compounds are very slowly eliminated, remaining stored in the system producing at times cumulative effects. Since the organic arsenicals are more readily eliminated, their structure should be such as to render them slowly soluble, securing thereby a slow protracted action. The aim in

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[1] Chemotherapie der Spirillosen-Ehrlich. Ber. 42, 17.

the study of the organic derivatives of arsenic acid has been to find products free from cumulative and secondary effects and adapted for hypodermic and intravenous use, avoiding thereby any derangement of the digestive tract. The newer and more successful products of this class are substituted arsenic acid derivatives of para-aminophenol, securing thereby a stable ring system from which the arsenic is liberated very slowly, producing a more continuous, less toxic and irritating action. Atoxyl, one of the first of this class to be introduced, was found to be more satisfactory than inorganic arsenic. While a greater percentage passed unchanged through the body, yet sufficient underwent some alteration in the system with the production of new synthetic types which were active in the destruction of these parasites. Ehrlich considers that in therapeutic action, benzene derivatives contain two different pharmaco-dynamic radicles, of which one acts as salt forming (—OH,—NH_2) and an increased action must result when a third group is introduced in the ortho- position to the salt forming radicle. Pentavalent arsenic compounds are secondary in spirilloidal power, and large doses are necessary with but little danger of optical atrophy. Many organic compounds of arsenic have been synthesised and tried clinically[1]: more successful commercially are arsacetin, arsylin, atoxyl, and arrhénal. Atoxyl gained a considerable reputation as a remedy in syphilis and sleeping-sickness (trypanosomiasis), but its use was attended frequently by degeneration of the optic nerve, leading to blindness, hence the attempt at acetylation (arsacetin), such as was done with aniline in converting into acetanilide.

As already stated, Ehrlich's experiments with atoxyl in treating trypanosoma infection culminated in his discovery of salvarsan which is likewise of value in malaria, leprosy, framboesia, as well as being a specific in syphilitic affections. The alkalinity of salvarsan corresponds to that of the blood, and its relative low toxicity in comparison with other arsenicals is due to its insolubility in the blood. Owing to the frequent occurrence of thrombosis arising from faulty neutralisation of salvarsan a soluble derivative has been prepared by precipitating a salt of 3:3′-diamino-4:4′-dihydroxyarsenobenzene with sodium methanal-sulphoxylate and dissolving the precipitate in alkali. This is called *neosalvarsan*. (Sodium 3:3′-diamino-4:4′-dihydroxyarsenobenzene-methanal-sulphoxylate

$NH_2\cdot C_6H_3(OH)As_2\cdot C_6H_3(OH)NH(CH_2O)SONa)$

D. R. P. 245756. Hoechst.

The relationship of the simpler derivatives of arsenic acid will be noted from the formulæ:

$AsO(OH)_3$	$AsO(OH)_2CH_3$	$AsO(OH)(CH_3)_2$
Arsenic acid	Methyl arsenic acid	Dimethyl arsenic . acid

$AsO(CH_3)_3$
Trimethyl arsenic acid

$AsO(OH)_2C_6H_4NH_2$	$C_6H_4NH_2\cdot AsO(OH)ONa$
Aniline arsinate	Aminophenyl arsinate of sodium (atoxyl)

Arrhénal. Methyl disodium arsenate
$AsO(CH_3)(ONa)_2,6H_2O$, m.p. 130°–140°, Merck.

Arsacetin. *p*-Acetylamino-phenyl-sodium arsenate $CH_3CO\cdot NH\cdot C_6H_4(AsO)OH\cdot ONa$
Hoechst.

Atoxyl. *p*-Aminophenyl arsenate of sodium
$NH_2\cdot C_6H_4\cdot AsO(OH)ONa\cdot 3H_2O$
Charlottenburg.

Asyphil, the mercury salt of atoxyl
Charlottenburg.

Cacodylic acid. Dimethyl arsenic acid, its salts with metals, guaiacol and alkaloids.

Soamin. Sodium arsanilate
$C_6H_4(NH_2)AsO(OH)ONa+5H_2O$ Burroughs.

Salvarsan[1] ('606'). *p.p*-Dihydroxy-*m.m*-diaminoarsenobenzene
$HO(NH_2\cdot HCl)C_6H_3\cdot As:As\cdot C_6H_3(NH_2\cdot HCl)OH,2H_2O$

Owing to its insolubility, it is necessary to add a calculated quantity of caustic soda for the preparation of salvarsan.

(U. S. Pat. 986148; Eng. Pat. 13485), Hoechst.

SYNTHETIC CATHARTICS.

The close relationship existing between the phenols and the quinones (oxidation-products of phenols) is marked in their physiological properties, more especially in their stimulating to irritant action in the intestinal canal. This is also true of the naphthaquinones and anthraquinones. The hydroxyanthraquinones stimulate intestinal peristaltic action increasing in intensity with the number of hydroxyls present; thus trihydroxyanthraquinone (anthrapurpurin)

$(C_6H_4[CO]_2C_6H(OH)_3)$ [1:2:7]

produces severe colic through its action on the smooth muscular fibres. Best known in this respect are a number of *a*-hydroxy derivatives of methyl anthraquinone, present in the glucosidal form in such cathartic drugs as aloes, rhubarb, senna, cascara sagrada, frangula, &c. The synthetic polyhydroxyanthraquinones are more drastic cathartic than the natural emodin of rhubarb. This suggested closing of part of the hydroxyl hydrogens by acyl or alkyl radicles, which would serve to secure a slower decomposition in the intestinal canal. Too rapid absorption increases undesirable action on the kidneys. The closing of all hydroxyls in this manner gave inert products.

The first experiments in this direction were purgatol, a diacetylanthrapurpurin, and exodin, a mixture of the feebly active diacetyl tetramethyl ether of rufigallic acid (hexa hydroxyanthraquinone) with their acetyl pentamethyl ether. The cathartic action of phenol groups containing carbonyls, as noted among the anthraquinones, explains this action attributed to phenolphthalein, which, however, was discovered through accident. It may be added that phenolphthalein is to-day the most successful synthetic cathartic, because it is practically entirely eliminated unchanged from the system.

Exodin.[2] A mixture of 30 p.c. rufigallic hexamethyl ether, 23 p.c. diacetyl rufigallic tetramethyl ether, and 47 p.c. of acetyl rufigallic pentamethyl ether, m.p. 180°–190° (D. R. P. 151724), Schering.

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[1] Organic Arsenic Compounds, W. Martindale, 10, New Cavendish St., London. Also Chemistry of Synthetic Drugs, Percy May, p. 186.

[1] Chemistry, Pharmacy and Therapeutics of Salvarsan, Martindale and Westcott, London.

[2] Fernik. Apoth. Zeit. 19. 598.

Emodin. Trihydroxymethylanthraquinone $C_6H_4:[CO]_2:CC_6{\cdot}CH_3(OH)_3$.

Hormonal. See under Organo-Therapeutics.

Purgatol (purgatin). Diacetyl ester of anthrapurpurin, Knoll.

Peristaltin. A glucoside from *cascara sagrada*. G. C. I. Basel.

Phenolphthalein. Sold under such titles as purgen, purgolade, purglets, laxan, laxol, &c.

ORGANO-THERAPEUTIC AGENTS.

Opo-therapeutics or animal remedials. One of the first to call attention to this class of remedial agents was Brown-Séquard, who advanced the hypothesis that 'all glands of the body, whether they have excretory canals or not, give to the blood useful principles, the absence of which is felt when these glands are extirpated or destroyed by disease.' This hypothesis was extended to include various other organs; and it was found that when one of these was in a diseased condition an extract prepared from the same organ of a healthy animal, serves as a remedial agent. For example, myxœdema, cretinism and Basedow's disease are traceable to a diseased condition of the thyroid gland which fails to perform its normal functions, hence the administration of extracts of this gland in treatment of these diseases. A tubercular affection of the supra-renal gland causes a malignant form of Addison's disease, now treated by suprarenal extracts. This same theory has been extended to include the thymus gland, the testicles, spleen, ovaries, spinal cord, brain, &c.

With few exceptions, the chemical nature of the organic principles which are present in these secretions is but little known, owing to minute quantities present and difficulties encountered in isolation. These remedials are sold in either powder or extract form. Owing to dangers arising from putrefactive changes, the organs are removed from freshly slaughtered animals (principally sheep, cattle and swine), thoroughly cleansed, and handled under aseptic conditions. They are either expressed, the juice being collected, mixed with lactose and dried at lowest possible temperature, or the entire organ is sliced and dried, or liquid extracts are prepared by digesting the sliced organ in a sterilised mixture of glycerol and water or salt solution or fatty oil. Since these secretions are of a basic character they readily form double or soluble compounds with sodium chloride. One part of Poehl's opotherapeutics represents 5 parts of the fresh organ. The other dry preparations are standardised in a like manner.

Suprarenal preparations.[1] Extracts or preparations from the suprarenal glands cause a contraction of the arteries with a corresponding increase of blood pressure. Locally, they produce ischæmia, through powerful contraction of the smaller blood vessels, and are chiefly employed in conjunction with local anæsthetics. The vaso constrictor action of these preparations is used to intensify and prolong the anæsthetic effect of local anæsthetics by retarding the circulation in affected parts and preventing the dilution of the local anæsthetic by too rapid absorption into the blood.

Adnephrin solution. A sterile 1 to 1000 solution of the suprarenal active principle in physiological salt solution containing 0·5 p.c. of chloretone. Stearns.

Adrenal-Poehl. A crystalline base from the suprarenal gland which is sold in 2 p.c. and 1 to 1000 solutions. Poehl.

Adrenaline (Takamine). Orthodihydroxyphenyl-ethanol methylamine hydrochloride: a lævorotary white crystalline base (m.p. 205°) obtained from the suprarenal glands.[1] Parke Davis.

Adrin (epinephrin hydrate). Solutions of active principle prepared according to method of V. Fuerth (Zeitsch. physiol. Chem. 26, 18). Mulford.

Arterenol $(OH)_2C_6H_3{\cdot}CH(OH)CH_2{\cdot}NH_2{\cdot}HCl$. The hydrochloride of *o*-dihydroxyphenyl-ethanolamine. A white crystalline powder, m.p. 141°; prepared synthetically. Hoechst.

Epinephrine $(OH)_2C_6H_3{\cdot}CH(OH)CH_2{\cdot}NH{\cdot}CH_3$ orthodihydroxy-4-methylaminoethanol benzene. Active crystalline principle first isolated by Abel from suprarenal glands.

Epirenan. Identical with adrenaline. Byk.

Hemisine. Identical with adrenaline. Burroughs.

Homorenon $(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2NH(C_2H_5){\cdot}HCl$. The hydrochloride of ethyl-amino-aceto-pyrocatechol. Colourless acicular crystal, m.p. 260°. Prepared synthetically: a 5 p.c. homorenon solution is equivalent to a 1 to 1000 adrenalin or suprarenin. Hoechst.

Suprarenalin. Identical with epinephrine. Armour, Chicago.

Suprarenin (synthetic[2]) $(OH)_2C_6H_3{\cdot}CH(OH)CH_2{\cdot}NH(CH_3)HCl$ ortho dihydroxyphenyl-ethanol-methylamino-hydrochloride. A white crystalline powder, m.p. 210°–212° (HCl salt, m.p. 161°). Lævorotary, synthetic, identical with adrenalin. Hoechst.

Suprarenin. A sterile solution of the active principle of the suprarenal gland. Hoechst.

Preparations of the suprarenal glands are:

Ext. glandulæ suprarenalis, an aqueous extract.

Glandulæ suprarenales sic, dried gland 1 : 5.

Paranephrin (Merck), a sterile purified extract.

Rachitol (Merck), dried glands.

Renoform. A solution of active principles. Freund.

Supradin. Iodised dried gland. La Roche.

Suprarenaden. An extract of gland. Knoll.

Opo-suprarenalin. A liquid extract. Poehl.

Chemically related to the suprarenal preparations, but reducing blood pressure less than adrenaline is *Tyramine*, *p*-hydroxy-phenyl-ethylamine hydrochloride $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2,HCl$, m.p. 268°-270° (Eng. Pat. 1560), a synthetic base discovered by Barger (Apoth. Zeit. 1909, 886) in ergot. Its action is similar, though feebler and more prolonged than that of adrenaline; produces uterine contractions and is not hæmostatic. Burroughs.

Thyroid preparations. Employed in psoriasis, lupus, exophthalmic goitre, myxoedema, obesity, &c. The glands from freshly slaughtered sheep are used. Most important are:

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[1] Review of literature, see Adrenalin and Adrenalin-like Bodies, Hygienic Laboratory, Bulletin No. 55, Washington, D. C.

[1] U.S. Pats. 730175–6, 730196–7–8, 753177.

[2] D. R. P. 152814–157300.

Iodothyrine, thyroiodine (thyrein). A milk sugar trituration of the active principle of the thyroid gland containing 0·0003 grm. of iodine to 1 grm., representing 1 grm. of the fresh gland (U. S. Pat. 626648). Bayer.

Thyreoidin. The dried gland, 0·6 grm. of which represents a fresh gland. Prepared by Merck, Poehl, Notkin, Burroughs.

Other similar preparations are *thyraden* (Knoll), *gland thyreoidæ sic, thyradol, thyrcoprotid* and *thyron.*

Serums from animals immunised against the thyroid toxine or those from which the gland has been removed.

Antithyreoidin (thyreoid serum), moebine. Merck.

Rodagen. Prepared from milk of thyroid extirpated goats. Charlottenburg.

Thyreoidectin. Red-brown powder. Parke Davis.

Hormone Therapy. A term used by Starling (Zentr. Physiol. Pathol. des Stoffwechels, 1907, 5, 6) to designate a group of physiological chemical substances (chemic reflexes), produced by certain cell groups, which, conducted by the blood to various parts of the body, stimulate certain cell complexes to specific functions. It has been shown that the spleen of animals elaborates in sufficient quantity for isolation a hormone which specifically stimulates intestinal peristaltis when employed intravenously. This is sold as

Hormonal. Liquid extract obtained from the spleen of an animal killed during digestion (U. S. Pat. 1034528). Schering.

MISCELLANEOUS ORGANO-THERAPEUTIC AGENTS.

Bone marrow preparations. Used in anæmia and chlorosis. *Medulla ossium rubra sic,* (Merck), *Medulladen* (Knoll), *Opomedullin* and *Opoossinum* (Poehl).

Brain preparations. For neurasthenia, hysteria, psychosis, diseases of nervous system. Prepared from gray matter of calves' brains. *Cerebrum siccatum* (Merck), *Opocerebrinum* (Poehl) and *Cerebrin.*

Liver preparations. For atrophic cirrhosis of liver, diabetes, hemeralopia, cholelithiases, &c. Heparaden (Knoll), Hepar sicc. (Merck), Opohepatoidin (Poehl), Heparon.

Ovaries preparations. For amenorrhæa, consequences following removal of ovaries. Oophorin (Dr. Freund, Berlin), Ovaria sicc. (Merck), Ovarinum (Poehl), Ovaraden (Knoll), Ovadin (La Roche), Ovariinum sicc. and lutein.

Mammary gland preparations. For menorrhagia, metrorrhagia, uterine fibroma, &c. Mammæ sicc. (Merck), Mammin and Opomammin (Poehl).

Pituitary body preparations. Used as cardiac tonic. Hypophysis cerebin sicc. (Merck), Opohypophysin (Poehl). Pituitrin (P. D. & Co.). Pituglandol (La Roche).

Spleen preparations. For anæmia, myxoedema, leucocythæmia, rachitis, enlarged spleen, &c. Lien sicc. (Merck), Lienaden (Knoll), Linadin (La Roche), Opolieninum (Poehl), Stagnin (Freund), Splenin and Splenon.

Testicle extracts: Orchitic fluid. For neurasthenic conditions and disturbances due to auto-intoxication. A tonic stimulant for entire nervous system. Didymin (Burroughs, Wellcome), Orchidin, Orchipin, Opoorchidin (Poehl), Spermin (Merck), Spermin-marpmann, Testes sicc. (Merck), Testaden.

Thymus gland preparations. For scrofula, Basedow's disease and pseudo-hypertrophy of the muscles. Glandulæ thymus sicc. (Merck), Opothymiium (Poehl).

Kidney preparations. Employed chiefly in nephritis. Renes sicc. (Merck), Renaden (Knoll), Renoform (Freund and Redlich, Berlin), Oporenin (Poehl). V. C.

SYRINGIN *v.* GLUCOSIDES.

SZMIKITE. Native monohydrated manganous sulphate $MnSO_4,H_2O$ (Schröckinger, J. M. 1877, 729).

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TACAMAHAC *Tacamahacin v.* OLEO-RESINS.

TACHHYDRITE $CaCl_2 \cdot 2MgCl_2, 12H_2O$. A mineral occurring in the salt deposits of Stassfurt in roundish, yellow, deliquescent masses.

TACHIOL *v.* SYNTHETIC DRUGS.

TAGUA NUT. The stony seeds of several species of the South American genus of palms, *Phytelaphas,* are known as tagua-nuts and are worked as 'vegetable ivory.' The two species mainly affording the commercial product are *P. macrocarpa* (Ruiz et Pav.) and *P. microcarpa* (Ruiz. et Pav.).

TA-HONG. A lead glass containing ferric oxide, used by the Chinese as a red enamel on porcelain.

TAIGU WOOD. A wood from Paraguay, resembling guaiacum wood in appearance. Has a greenish-brown colour when fresh; becomes covered on exposure to the air with a greenish-yellow crystalline powder; and exhibits under the microscope yellow oblique prisms, together with shining, colourless, thin six-sided tables. The latter are not altered by alkalis; the former, which consist of *taiguic acid,* are reddened thereby. Strong boiling alcohol extracts from it 13·7 p.c. of a mixture of taiguic acid with resinous and waxy substances. Taiguic acid $(C_4H_4O)_n$ crystallises in oblique prisms of a bright-yellow colour; is tasteless and odourless; m.p. 135°, and sublimes at 180°. Very slightly soluble in water, except under pressure; readily soluble in acetone, ether, benzene, or strong alcohol. Forms crystallisable salts with bases; those with the alkalis are deep red and easily soluble in water, the lead salt is yellow, and the silver salt cinnabar-coloured (Arnaudon, J. 1858, 264).

TALC (Ger. *Talk*). A mineral species consisting of hydrogen magnesium silicate

$$H_2Mg_3Si_4O_{12}$$

occurring as foliated or compact masses. The name, said to be from the Arabic 'talq,' has no doubt long been applied to a variety of foliated minerals, such as mica and gypsum; and even at the present time it is sometimes used as a popular name for mica. The term *steatite* (Ger. *Speckstein*) is restricted to the compact, massive varieties of talc. *Soapstone* and *potstone* are impure forms of steatite; but, like the name agalmatolite (*q.v.*), they are more general in their application, and no doubt include minerals of other kinds.

Talc never occurs as distinct crystals, but only as folia or scales, which possess a perfect micaceous cleavage and a pearly to silvery lustre on their surface. The folia are flexible but not elastic, thus differing from mica. Talc is extremely soft and can be readily scratched with the finger nail; it is chosen as No. 1 in Mohs's scale of hardness. The massive varieties are often rather harder, and may range up to 2½–4 on the scale; but they are usually sufficiently soft to be readily cut with a knife and carved. A very characteristic feature of the mineral is its greasy or soapy feel. The colour of foliated talc is silvery-white or often a delicate shade of green; steatite is creamy-white, greyish, or greenish; and potstone and soapstone are of darker shades of colour. Sp.gr. 2·6–2·8. The mineral is very resistant to heat (no water being lost below a red-heat), to acids and to solutions of alkalis.

Analyses: I. Green, foliated talc from Tyrol (Scheerer, 1851). II. Fibrous talc ('agalite') from Edwards, St. Lawrence Co., New York (E. S. Sperry in Dana's System of Mineralogy, 1892). III. Pseudomorphous steatite from Göpfersgrün, Wunsiedel, Bavaria (Scherrer, 1851). IV. Steatite from Hewitt mine, Swain Co., North Carolina (J. H. Pratt, Economic paper No. 3, North Carolina Geol. Survey, 1900). V. Soapstone from Grafton, Vermont (G. P. Merrill, The Non-Metallic Minerals, 2nd ed., New York, 1910). VI. Soapstone from Francestown, New Hampshire (G. P. Merrill, *l.c.*).

	I.[1]	II.	III.	IV.[2]	V.	VI.[3]
SiO_2	62·12	60·59	62·35	61·35	51·20	42·43
Al_2O_3	—	0·13	trace	4·42	5·22	6·08
FeO	1·58	0·21	1·34	1·68	8·45	13·07
MnO	—	1·16	—	—	0·32	trace
CaO	—	—	—	0·82	1·17	3·27
MgO	31·15	34·72	31·32	26·03	26·79	25·71
H_2O	4·73	3·77	4·78	5·10	6·90	8·45
Total	99·82	100·58	99·79	100·02	100·05	99·49
Sp.gr.	2·69	2·908	—	—	—	—

Talc is of wide distribution, occurring more especially in schistose rocks and those of metamorphic origin (*e.g.* talc-schist). It is a common alteration-product of many minerals, and in the impure, massive form is intermingled with other secondary and residual products (chlorite, mica, &c.). Distinctly shaped pseudomorphs after various crystallised minerals are not uncommon.

Workable deposits, forming veins, beds, and lenticular masses, are found at many localities. Veins of steatite in the serpentine of the Lizard district in Cornwall were formerly worked for supplying material used in the manufacture of old Worcester porcelain. At Göpfersgrün near Wunsiedel in the Fichtelgebirge, Bavaria, important deposits of steatite occur at the junction of granite and limestone; the latter and its contained minerals having been largely altered by magnesium-bearing solutions emanating from the granite. Deposits are also worked in the Pyrenees and in the Italian and Austrian Alps. The best qualities for toilet and medicinal purposes have long been obtained near Pinerolo in the Chisone valley, Piedmont. At several places in India large quantities of steatite and potstone are quarried for carving into bowls, plates, cups, and other domestic utensils and ornamental objects. The largest amounts (about 120,000 tons per annum) are obtained in the United States. The fibrous talc ('agalite,' *q.v.*), which occurs as an alteration-product of tremolite and enstatite in crystalline limestones, in the Gouverneur district, St. Lawrence Co., New York, is employed in large quantities in the manufacture of writing and printing papers. Steatite and soapstone are obtained from Virginia, North Carolina, Vermont, &c.

The uses of talc are many. Powdered talc enters largely into the composition of toilet-powders; it is used as a dry lubricant; for dressing leather, cloth, rubber, &c.; for foundry facings; for adulterating soap and other goods; in the manufacture of paper and paints (enamel paints, and especially those for preserving the iron work of bridges and ships); as a non-conducting material for covering steam-pipes; as a preservative coating on stone work. Steatite (the well-known 'French chalk') is used for marking on cloth, metal, glass, slate, and blackened paper. It forms the tips of gas-burners, backs of stoves, furnace linings, &c. Being soft and readily worked, it is a favourite material for elaborate carvings, especially in the East. It has also been used as a source of magnesium salts, particularly the sulphate. Sawn slabs of soapstone are extensively used in America for benches (in chemical laboratories, hospitals, &c.), acid tanks, sinks, laundry tubs, hearth-stones, foot-warmers, and even for building purposes. Being a good insulator, it is used for electrical switchboards, and the floors of generating stations.

Another mineral also applied to many of these purposes is pyrophyllite ($H_2Al_2Si_4O_{12}$) (*q.v.*; *v.* also AGALMATOLITE).

References. On American talc and soapstone *v.* G. P. Merrill, The Non-metallic Minerals, 2nd ed., New York, 1910. R. H. Vail, Mineral Industry, 19, New York, 1911. J. S. Diller, Mineral Resources of the United States (U. S. Geol. Survey), ii. 1911. J. H. Pratt, Talc and Pyrophyllite Deposits in North Carolina, Economic Paper, No. 3, N. C. Geol. Survey, 1900. On Indian steatite *v.* G. Watt, Dictionary of the Economic Products of India, 6, 1893. L. J. S.

TALIPOT. A variety of starch obtained from a palm, *Corypha umbraculifera* (Linn.). Known in Ceylon as 'raw palmira root flour.'

TALLOW. In commerce a distinction is made between *beef* tallow and *mutton* tallow. The former is obtained from oxen, cows, and calves; the latter from sheep and goats. The distinction is, broadly speaking, supported by chemical differences in the composition of the respective triglycerides, mutton tallow being as a rule richer in stearin than beef tallow.

The quality—especially the hardness—of tallow depends on the breed and the age of the animal, and to some extent on the food. The fat from the male beast is generally harder than that obtained from the female. Animals fed on grass yield a harder fat than those fed with

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[1] Also NiO, 0·24.

[2] Also Na_2O, 0·62.

[3] Also Na_2O, 0·16; K_2O, 0·32.

oilcakes; brewery refuse produces especially soft tallow. Hence we have all gradations from the hard South American beef tallow to home-melt tallow of somewhat softish consistence.

The 'rough fat' is delivered with the adhering tissue, &c., to the tallow-melters, and is rendered at a temperature of about 100° (*see Rendering* under Oils, Fixed, and Fats).

The fats from different parts of the carcase, although of unequal value, are not kept separate, unless the fat be intended for the manufacture of oleomargarine or of tallow of best commercial quality.

At present the tendency prevails to collect the rough fat, as far as possible, in large rendering establishments fitted up with modern appliances. Hence the slaughter-houses in large towns—especially on the Continent of Europe—have at present as an adjunct a tallow-rendering establishment. These are found on the most gigantic scale in the large packing-houses of the United States of America as also of South America.

For the production of tallow for the manufacture of margarine the more valuable kidney fat ('suet,' 'edible fat') and bowel fat ('midgerum fat') is dealt with separately and not mixed with the caul- (or kell-, *i.e. omentum*) fat and the fat from other parts of the carcase.

By melting this selected fat at low temperatures—not exceeding 50°—the 'premier jus' is obtained (*see* Margarine).

The following commercial brands of tallow are differentiated :—

(1) Rendered tallow, which contains all the fat from the carcase.

(2) 'Premier jus.'

(3) Pressed tallow (tallow stearine, beef stearine, mutton stearine, oleostearine).

(4) Oleomargarine, oleo oil.

The first named quality of tallow, viz. 'rendered tallow,' is frequently expressed in hydraulic presses for the preparation of 'tallow stearine' and 'tallow oil.'

It is almost impossible to estimate the quantity of home-melt tallow produced in European countries, as the production is scattered over the smallest establishments, embracing even those of butchers in villages.

None of the European countries is at present exporting tallow, the quantities exported from the United Kingdom being in fact re-exports. Russia, which up to about two decades ago was a tallow-exporting country, has been forced to draw upon the world's supply for her own demands. Even the United States of North America, which for many years have been large suppliers of tallow, have practically ceased to export tallow, they themselves importing tallow from South America.

The chief sources of tallow—in addition to the 'home-melt' productions—are at present Australasia, South America, and to a smaller extent New Zealand. Large quantities of tallow are expected in the near future from Rhodesia.

The imported tallows are chiefly of the quality enumerated above under No. 1, viz. rendered tallow containing all the fat from the carcase. These tallows are sold according to their titer (titre), solidifying point of fatty acids and colour (*see* Oils, Fixed, and Fats).

As regards colour the commercial brands are differentiated as 'good colour,' 'off colour,' 'no colour,' &c., and are merely judged by the standards agreed upon between sellers and buyers on the London market. There is a further distinction made between 'beef,' 'mutton,' and 'mixed' tallows.

During recent years, in consequence of the great demand for edible fats, the production of 'premier jus' for export to Europe has been established on a large scale in oversea countries. Such tallow is not only carefully prepared from selected rough fat, but it is also filtered over fuller's earth, so that it arrives in a perfectly sound state in Europe When carefully packed, it will keep for months in good condition. Thus the production of oleomargarine and oleostearine for export to Europe has assumed considerable dimensions during the last few years.

On pressing tallow for the production of 'stearine,' *tallow oil* is obtained as a by-product: this is liquid or semi-solid according to the temperature at which it has been expressed. Tallow oil is chiefly used in admixture with mineral oils as a lubricating oil. Its solidifying and melting-points, as also its iodine values, naturally vary according to the conditions under which the tallow has been expressed.

Beef tallow. (For characteristics *see* Oils, Fixed, and Fats.) Beef tallow when freshly rendered is nearly white, free from disagreeable odour, and almost tasteless. Such quality is represented by 'home-melt beef tallow.' Imported tallow passes through all gradations, from 'bleached' white to slightly yellowish tallow (Australian), through darker yellow (North American, South American) to, finally, the 'off-coloured' lowest grades (North American, Australian 'no colour').

Tallow was until recently considered to consist exclusively of the glycerides of palmitic, stearic, and oleic acids. The amount of olein used to be calculated from the iodine value. It is not unlikely that owing to the influence of vegetable oils given with the food (oilcakes, &c.) less saturated acids than oleic acid may be found.

Boemer has shown that by frequently repeated crystallisation of tallow from ether, approximately 1½ p.c. of pure tristearin can be isolated.

On the assumption that the fatty acids of tallow consist of palmitic, stearic, and oleic acids only, the composition of a sample may be arrived at by determining the proportion of stearic acid (*see* Oils, Fixed, and Fats). The proportion of oleic acid can be calculated from the iodine value; the difference gives then the amount of palmitic acid.

Beef stearine is the hard portion of tallow left in hydraulic presses after removal of the tallow oil (*see* above). Boemer has shown that by frequently repeated crystallisation of beef stearine from ether, approximately 4·5 p.c. of pure tristearin can be isolated. Beef stearine obtained from 'premier jus' is used for edible purposes in the manufacture of margarine, as also in the manufacture of compound lards and in the preparation of 'suet substitutes.'

The amount of free fatty acids in tallow varies considerably with the state of purity. In freshly rendered tallows, the proportion of free fatty acids is negligible and rarely exceeds 0·5 p.c.; in commercial samples, the percentage of free fatty acids may rise to 25 p.c. and even more.

For the complete commercial examination of tallow, *see* Lewkowitsch, Chem. Tech. ii. 640.

Mutton tallow. (For characteristics, *see* OILS, FIXED, AND FATS.) Mutton tallow closely resembles beef tallow; it is frequently mixed with the latter and is then sold as 'mixed tallow.' Mutton tallow is, as a rule, harder than beef tallow, and consequently its solidifying and melting points, as also those of its fatty acids, are higher. It is more liable to turn rancid than beef tallow. For this reason it cannot be used in the manufacture of first-class butter-substitutes or high-class toilet soap.

Boemer has shown that by frequently repeated crystallisation of mutton tallow from ether approximately 3 p.c. of pure tristearin and 4–5 p.c. each of stearodipalmitin and palmitodistearin can be isolated. J. L.

TALMI GOLD. An alloy of 86·4 p.c. copper, 12·2 p.c. zinc, 1·1 p.c. tin, and 0·3 p.c. iron, used in the manufacture of trinkets.

TA-LOU. A Chinese term for a glass flux used for enamelling on porcelain. Consists mainly of a lead silicate containing a small quantity of copper (Ebelmen and Salvétat, Ann. Chim. Phys. [iii.] 35, 344).

TAMBAC or **TOMBAC.** *White copper.* An alloy of 85 p.c. copper and 15 p.c. zinc.

TANACETONE *v.* KETONES.

TANGHIN or **TANGUIN.** The celebrated judicial poison used by the inhabitants of Madagascar has been examined by Arnaud. It was known that the toxic principle was contained in the almonds of the *Cerbera Tanghin* (Hook.) belonging to the family of the *Apocynaceæ*. The almonds contain about 75 p.c. of fatty matter which could not be got rid of by simple pressing. By treating with carbon disulphide, however, which does not take up the tanghinin, the fat was extracted. Subsequent boiling with strong alcohol, and evaporation, yield a crystalline substance of powerful toxic properties. It has a strong action upon the heart, resembling strophanthin and ouabaïne (J. Soc. Chem. Ind. 1889, 211; 1888, 765), having, however, a more general convulsive action than these bodies.

Tanghinin forms colourless, rhombic, anhydrous crystals which melt at 182°, and are very sparingly soluble in water, but easily in strong alcohol. It is lævorotatory, and has the following composition: Carbon, 65·74; hydrogen, 8·19; oxygen, 26·07 (Arnaud, Compt. rend. 1889, 108, 1255; *ibid.* 109, 701).

The poisonous properties of a tanghin or ksopo extracted from the plant *Menabea venenata* (Baill.) of the family *Asclepiadeen* and used by the Sakalaves, are described by Camus (Compt. rend. 1903, 136, 176).

TANNASE. A diastase found in nut-galls, sumac leaves, &c., capable of hydrolysing tannin (Fernbach, Compt. rend. 131, 1214; Poltevin, *ibid.* 131, 1215).

TANNASPIDIC ACID *v.* FILIX MAS.

TANNING *v.* LEATHER.

TANNINS (*Acides tanniques*, Fr.; *Gerbstoffe*, Ger.). This term has been applied to a large class of substances which have been found in many plants and are distinguished by the following characters: they have an astringent taste; give a blue-black or green coloration with ferric salts; are precipitated by a solution of gelatin, by albumen and by alkaloids; unite with hide to form leather.

It was formerly believed that only one tannin existed, and it was assumed that the difference in properties of tannin from different sources was due to the presence of foreign matter. It is, however, now well known that tannin from different sources frequently differs both in composition and in properties, and although it is probable, owing to the difficulty of obtaining these compounds in an even approximately pure condition, that the number of distinct individuals may not be so great as is usually supposed, there can be no doubt that at least three important classes of tannins exist in nature. The earliest suggestion was to divide the tannins into two classes—the iron-blueing tannins, and the iron-greening tannins—according to their behaviour towards salts of iron, and it was considered that whereas the former were pyrogallol compounds, that the latter were derived from catechol. This differentiation appears in the main to be correct, and the employment of ferric chloride for this purpose, or better iron alum as a preliminary step, is of general application; but on the other hand, it is to be borne in mind that the presence of acid, alkali, or organic impurity has considerable effect upon the colour production. Thus, although the method is no doubt of service in many cases even with the plant infusion, its exact significance can only be ascertained from the coloration given by the purified tannin itself.

Stenhouse (Proc. Roy. Soc. 11, 405) believed that those tannins which give blue-black precipitates with ferric salts are mostly glucosides. Wagner (Zeitsch. anal. Chem.) made a distinction between *pathological* and *physiological* tannins and considered that the former class represented by gallotannic acid only existed in pathological formations of certain species of oak and sumac [*Rhus javanica* (Linn.) and *R. semilata* (Murr.)], whilst the latter class include all tannins which are produced under normal conditions of plant life. As, however, gallotannic acid has been found to exist in some plants as a physiological tannin, Wagner's classification is untenable.

Böttinger (Ber. 1884, 17, 1123) has examined the action of bromine on aqueous tannin extracts, and determined the percentage of bromine contained in the precipitated bromo products. As a result, it was shown that certain tannins may be grouped together according to the amount of bromine which they take up.

Hemlock bark tannin . .	43·6
Quebracho tannin . . .	44·5
Mangrove tannin . . .	42·15
Mimosa tannin . . .	49·36
Chestnut oak tannin . .	50·48
Terrajaponica tannin . .	53·2
Spruce bark tannin . .	52·8

A very large amount of attention has been given to the classification or identification of aqueous extracts of tanning materials, by the coloured and other effects given by certain reagents. It remains to be decided whether in all cases these reactions in reality arise from the tannin itself.

The more important methods which may be used to classify the tannins into groups, according to our present knowledge of these substances are as follows:—

Coloration with ferric chloride or iron alum (see above).

Digestion with boiling dilute sulphuric acid. In this method of procedure, three definite reactions are observed: (*a*) the hydrolysis of the tannin with formation of gallic acid (gallotannic acid); (*b*) the precipitation of ellagic acid (ellagitannic acid); (*c*) the gradual production of an amorphous red-coloured precipitate known as a 'phlobaphene' (catechol or phlobatannin).

Precipitation with bromine water indicates the presence of a so-called catechol or phlobatannin (Procter, Leather Industries Handbook, 1898).

Pine wood and hydrochloric acid test. If a deal shaving be moistened with a solution of phloroglucinol and then with strong hydrochloric acid, a deep red-violet colour due to the formation of phloroglucinol vannillein is produced. Resorcinol reacts similarly giving a blue-violet (Procter). These colorations are an indication of the presence of a phloroglucinol or resorcinol nucleus in the tannins. Gallotannin and ellagitannin solutions do not react in this manner.

Diazobenzene chloride. Solutions of certain tannins in the presence of alkali or alkaline acetates give a red coloured precipitate of the azobenzene tannin with this reagent, a fact which indicates with some certainty the presence of a phloroglucinol or resorcinol grouping. Gallotannin and ellagitannin do not react in this manner.

Fusion with alkali. Procter (Leather Industries Handbook, 1898) recommends adding 20 grms. of tannin to 150 c.c. of a solution of potassium hydroxide of sp.gr. 1·20 and concentrating the liquid during 3 hours until it becomes pasty. Or 5 to 10 parts of caustic potash and a few drops of water are heated with one part of the tannin to 210°–240° for 20 minutes. Gallotannin, by this method, gives gallic acid, and possibly traces of pyrogallol, whereas the so-called catechol tannins yield protocatechuic acid or other allied acid, alone, or together with phloroglucinol or resorcinol, &c.

Heating with glycerol. The tannin (1 grm.) is heated with 5 c.c. of glycerol slowly raising the temperature from 160°, and keeping it for half an hour between 200°–210°. The product diluted with 20 c.c. of water is extracted with ether, the extract evaporated and the residue tested for pyrogallol or catechol. According to Trimble (The Tannins), paraffin wax may be employed in place of glycerol.

Formaldehyde test. When an aqueous solution of a so-called catechol tannin is treated with formaldehyde and a little hydrochloric acid and gently warmed the tannin is completely precipitated. Pyrogallol tannins do not yield an entirely insoluble compound in this manner. This reaction, discovered by Stiansy (Der Gerber, 1905, 185), has by numerous writers been assigned to Jean and Frabot (Ann. Chim. anal. 1907, 12, 49).

Lead acetate test (Stiasny and Wilkinson, Collegium, 1911, 475 (2 ix.) 318). All natural tannins are completely precipitated by lead acetate solution in so far as the filtrate from the precipitate does not give the iron test. In the case of catechol or phlobatannins this precipitate is dissolved by dilute acetic acid, whereas with the gallotannins the lead com-ound is insoluble or but partially soluble. The is preferably made by adding 10 c.c. of acetic acid (10 p.c.) to 5 c.c. of the tannin solution, and then adding 5 c.c. of lead acetate (10 p.c.). No precipitate is thus produced in the case of the catechol or phlobatannins.

By these methods it is easy to divide the tannins into three classes, usually distinguished as (1) gallotannins, (2) ellagitannins, and (3) catecholtannins. Since the discovery of synthetical tannins by Fischer and Freudenberg (Annalen, 1911, 384, 225), it is evident that this nomenclature, as applied to the first group, is imperfect. Thus, whereas the term 'gallotannin' is in reality only applicable to compounds containing pyrogallol nuclei and in fact merely relates to digallic acid and its derivatives, it is now known that diprotocatechuic acid, diresorcylic acid, and digentisic acid, members of the same group, possess tanning property. On this account it is considered more reasonable to distinguish such tannins by the term 'depside,' a nomenclature which is due to Fischer and Freudenberg, although it is not suggested that such a group is absent in the other tannins.

Again, as regards the so-called 'ellagitannin' group (2), new tannins belonging to this class may also be either synthesised or isolated in the future. The term 'ellagitannin' is therefore here replaced by 'diphenylmethylolid,' the name by which the group mother substance is known.

Exception is again to be taken to the designation 'catechol' tannin (3) for reasons similar to those given above and which are discussed later in this article, and this name is also replaced by 'phlobatannin,' in that these compounds, apparently without exception, possess the property of yielding phlobaphenes. In respect of this latter group, it is to be noted in connection with the qualitative tests above enumerated that the formation of phlobaphene and of precipitates with bromine water and with formaldehyde sufficiently indicate the presence of this variety of tannin, because these compounds may not all react with pine wood and hydrochloric acid, or diazobenzene chloride, or give protocatechuic acid as one of their decomposition products.

There appears to be ample evidence also of the existence of special varieties of glucoside belonging to this third class, distinguished by their extremely hygroscopic nature and the fact that they are insoluble or nearly so in acetic ether. They give, however, the well-marked reactions of the phlobatannins. None of these compounds has yet been obtained in a pure condition, but when they are digested with boiling dilute mineral acids a sugar and phlobaphene appear to be mainly produced.

Methods of isolation.

All the well-known tannins are dissolved by hot water, and yield precipitates with lead acetate solution, and thus by decomposing the well washed lead precipitate from a plant infusion in the moist condition with sulphuretted hydrogen a crude solution of the tannin is obtained. This can be concentrated *in vacuô* over caustic potash or sulphuric acid. In the place of lead acetate, stannous chloride was employed by Proust in 1798 (Ann. Chim. Phys. 25, 225), who is credited with being the first to prepare tannic acid in a nearly pure condition. As, however, the tannin usually exists in the plant side by side with yellow colouring matter, either in the free state or as glucoside, and other secondary substances soluble in water, a fractional precipitation with lead acetate is preferably adopted, in which case the middle portion usually yields the purest tannin (Grabowski, Sitz. Ber. 1867, 55, ii. 567; Trimble, The Tannins, 1892, i. 85). A preliminary treatment with lead acetate in the presence of a little acetic acid is serviceable in some cases for the precipitation of coloured impurities. Probably the solvent most extensively employed since 1880 in the investigation of tannins has been ethyl acetate, in which case it has been usual to agitate a solution of the substance or extract of the plant with this solvent. A preliminary addition of salt or sodium sulphate to the liquid is beneficial.

Certain tannin glucosides, owing to their sparing solubility in ethyl acetate, cannot be satisfactorily isolated in this manner, and the method is not applicable to the case of mineral salts of the tannin, in which the preliminary production and subsequent decomposition of the lead salt is to be recommended. Numerous methods have been adopted for the purification of the tannin thus prepared, and are given under the head of the special substance with which they have been employed.

In many cases it has been found preferable to extract the tannin matter with an organic solvent rather than with water. This is, as a rule, to be advised, as the crude substance is thus more readily isolated in a concentrated form. Indeed, one of the oldest methods of separating tannins from other substances is that of Pelouze (Ann. Chim. Phys. 1834, 55, 337), who exhausted powdered gallnuts with commercial ethers. Various mixtures of alcohol, ether and water have been recommended, and also dilute alcohol in the case of gallnuts for preparing gallotannic acid, although these methods must not be considered of special advantage for the isolation of tannins as a whole. Probably the most efficient solvent for general purposes of investigation is acetone which was employed by Trimble for the percolation of numerous tannin matters (The Tannins).

I. Depside Group.

Tannin, *Tannic acid*, *Gallotannin*, *Gallotannic acid* is found to the largest extent in galls which arise from the puncture of insects of the genus *Cynips* on the leaves and buds of various species of oak, more especially the *Quercus lusitanica* (Lam.), and on a species of sumach, *Rhus semilata* (Murr.). Aleppo galls, derived from the young shoot of the oak and which are the best variety of oak gall on the market, contain 50–60 p.c. of gallotannic acid, whereas Chinese galls from sumach yield as much as 70 p.c. In smaller amount it occurs also in numerous plants, and is probably the main tannin of various sumachs, of valonia, divi-divi, and algarobilla.

The methods employed for the isolation of gallotannic acid from galls are more or less modifications of that of Pelouze, which consists in extracting finely powdered galls with commercial ether. The extract separates into two layers, the upper consisting of an ethereal solution of gallic acid, wax, and resinous substances, whereas the lower represents a concentrated solution of gallotannic acid which, on evaporation, remains as a porous mass. In place of the ether, a mixture of 75 p.c. commercial ether and 25 p.c. alcohol, can be employed. The method of Leconnet (Annalen, 1836, 18, 179) consists in stirring powdered galls into ether until a thin cream results, pressing the mixture and repeating the operation until tannin is no longer removed. According to Domine (J. Pharm. Chim. 1844, [3] 5, 231), it is advantageous to allow the powdered galls before extraction to remain for some time in a moist atmosphere, and Pelouze's process with this modification was adopted by the British and United States pharmacopœias.

For the manufacture on the large scale, Chinese or Japanese galls are preferably employed owing to their richness in tannin. The finely powdered material is stirred with sufficient water at 50°–60° to form a concentrated aqueous extract, and after filtration the clear liquid is agitated with one-fourth of its volume of ether until an emulsion results. After standing for several days, the upper ethereal liquid which has separated is removed, and the lower layer, which contains all the tannin matter, is run into a still and the ether which is present recovered. After cooling the syrupy liquid is spread out on sheets of tin, and heated by means of a steam coil, when the gallotannic rapidly puffs up and dries.

Thus prepared the commercial tannin contains some quantity of gallic acid, plant wax, glucose and other impurities; to remove these the material may be washed with ether, or the aqueous solution shaken with ether, or the aqueous liquid fractionally precipitated with common salt, the precipitate dissolved in ethyl acetate, and the tannin recovered by evaporation under reduced pressure. Trimble (The Tannins, 85) treats a 5 p.c. solution of the tannin with 10 p.c. lead acetate, drop by drop, until the precipitate at first yellow coloured ceases to be granular and is colourless. This is collected, the filtrate agitated two or three times with ethyl acetate and the extract evaporated. The colourless product, which still contains gallic acid, is redissolved in water, and the solution, after agitation with ether, evaporated under reduced pressure. Finally, the residue dissolved in ether with a little water is again brought rapidly to dryness under reduced pressure, and thus obtained is colourless and gives no reactions for gallic acid or glucose. With the object of preparing a homogeneous product, Walden (Ber. 1898, 30, 3154) has employed dialysis, and also the precipitation of a solution of the purest commercial tannin in ethyl acetate with benzene. Rosenheim and Schidrowitz (Chem. Soc. Trans. 1898, 73, 882) point out the extreme difficulty of removing the last traces of gallic acid from the tannin and employ a mixture of ether and acetone for this purpose. Paniker and Stiasny (Chem. Soc. Trans. 1911, 9, 1821) state, however, that the process of Rosenheim and Schidrowitz only partially removes gallic acid The method suggested by Perkin, which consists in neutralising a solution of the tannin with sodium bicarbonate, extracting the mixture with ethyl acetate, and subsequently precipitating the substance from the extract with benzene, gives a product free from even traces of gallic acid (*see* also Iljin, Ber. 1909, 42, 1731). Fischer and Freudenberg (Ber. 1912, 45, 919) find the addition of dilute sodium hydroxide to the tannin solution until faintly alkaline before extraction with ethyl acetate is similarly beneficial.

Gallotannic acid as found in commerce consists of an amorphous powder possessing a faint yellow colour, although when exhaustively purified it is colourless. It is readily soluble in water and alcohol, more sparingly in ethyl acetate, insoluble in pure ether, chloroform or benzene. With solutions of ferric salts, gallotannic acid gives a bluish-black coloration or precipitate, according to the concentration, whereas ferrous salts give with strong solutions only, a white precipitate which gradually turns blue in the air. Many metallic salts give precipitates with the tannin, those of lead and tin being colourless whereas the copper and silver compounds possess a brown tint. Cold alkaline solutions absorb oxygen from the air and darken in colour with production of the so-called *metagallic acid.* When boiled hydrolysis occurs and gallic acid is formed. Gallotannic acid precipitates most alkaloids and gives precipitates with albumen and gelatin, the latter, according to Trunkel (Zeitsch. Biochem. 1910, 26, 458), in quantitative amount.

Analyses of gallotannin by Berzelius, Pelouze, Mulder, Bijlert, Strecker, Gautier, Trimble, Dekker and Walden have been in fairly close agreement, varying from about C=51·5 to C=52·3; H=3·7 to H=4·1 p.c. Iljin (Ber. 1909, 42, 1735) has suggested higher numbers (C=54·13; H=3·22), the correctness of which he has again emphasised (J. pr. Chem. 1910, [ii.] 82, 422; *cp.* Nierenstein *ibid.* 1909, 42, 3552). Mulder (J. pr. Chem. 1849, 48, 90) was the first to assign to gallotannin the formula $C_{14}H_{10}O_9$, and this was subsequently adopted by Schiff (Ber. 4, 231) and until recently generally accepted as correct. Very numerous salts of gallotannic acid have been described which are in fair agreement with this view, of which *ammonium tannate* $NH_4C_{14}H_9O_9$, *potassium tannate* $KC_{14}H_9O_9$, *sodium tannate* $NaC_{14}H_9O_9$, and *barium tannate* $Ba(C_{14}H_9O_9)_2$ (Buchner, Annalen, 53, 361) may be given as examples. For a complete list reference should be made to Beilsten (1896, ii. 1926).

Gallotannic acid isolated from plants is said to contain glucose which is difficult to eliminate. Strecker (Annalen, 90, 340) indicated the possible existence of a glucoside of the formula $C_{27}H_{22}O_{17}$, although Schiff (*ibid.* 170), while agreeing that unaltered tannin is probably a glucoside of digallic acid, preferred the formula

$$C_{34}H_{28}O_{22}(=C_6H_{12}O_6+2C_{14}H_{10}O_9-2H_2O).$$

This corresponds to a yield of 23 p.c. of glucose; in natural tannin about 22 p.c. has been detected.

When gallotannic acid is heated at from 160°–215°, water, carbon dioxide and *pyrogallol* are evolved, and a dark coloured non-volatile substance known as metagallic acid is produced. According to Trimble (*l.c.*) the best yields of pyrogallol are obtained by raising the temperature slowly to 215° and then keeping it between 190°–210° for half an hour. Digested with boiling dilute mineral acids, gallic acid is produced, and Wetherill, who employed for this purpose 50 grms. of tannic acid and 500 c.c. of sulphuric acid (1 vol. acid + 4 of water), obtained a yield of 87·4 p.c. of gallic acid. Knop (Annalen, 170, 44) obtained 95 p.c., and Stenhouse the theoretical amount, whereas Trimble (*l.c.*) states that when pure gallotannic acid is heated with a 2 p.c. solution of absolute hydrochloric acid, gallic acid only is produced. This reaction was formerly assumed to be expressed by the following equation

$$C_{14}H_{10}O_9+H_2O=2C_7H_6O_5.$$

Boiling alkaline solutions also produce gallic acid, but hot aqueous ammonia yields *ammonium gallate* and *gallamide* as follows:

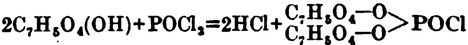
$$C_{14}H_{10}O_9+2NH_3=C_7H_5O_5NH_4+C_7H_5O_4NH_2.$$

According to Voswinkel (D. R. P. 1905), on adding formaldehyde to an aqueous solution of tannin and carbamide in molecular proportion, a precipitate of *methylene tannin carbamide* is formed

$$C_{14}H_{10}O_9+CO(NH_2)_2+H{\cdot}CHO$$
$$=C_{14}H_9O_9{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2+H_2O.$$

It is a yellow powder decomposing about 220° and is insoluble in organic solvents with the exception of alcohol.

By heating barium gallate with silver nitrate, Löwe (J. pr. Chem. 1867, 102, 111) obtained a substance resembling gallotannic acid, and the same compound, together with ellagic acid, was also produced by the action of arsenic acid on gallic acid. Schiff (Ber. 1871, 4, 231) found that when gallic acid was heated with phosphorus oxychloride at 100°, and subsequently at 120°, digallic acid was produced and this had the same percentage composition, and properties as natural gallotannin. The reaction (Annalen, 1873, 170, 56) most probably occurred as follows:

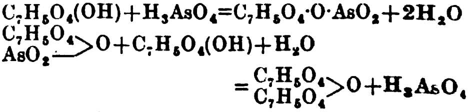


$$2C_7H_5O_4(OH)+POCl_3=2HCl+\begin{matrix}C_7H_5O_4-O\\C_7H_5O_4-O\end{matrix}\!\!>POCl$$

$$C_{14}H_{10}O_{10}{\cdot}POCl+4C_7H_6O_5$$
$$=3C_{14}H_{10}O_9+H_3PO_4+HCl$$

and there was indeed evidence of the intermediate formation of a phosphorus compound. Further, it was noticed that pure tannin gives some ellagic acid when heated with phosphorus oxychloride at 130°–140°. Schiff (Ber. 1871, 4, 967) also corroborated Lowe's statement that digallic acid is produced from gallic acid by means of arsenic acid. The reaction could be expressed thus:

$$C_7H_5O_4(OH)+H_3AsO_4=C_7H_5O_4{\cdot}O{\cdot}AsO_2+2H_2O$$



$$\begin{matrix}C_7H_5O_4\\AsO_2\end{matrix}\!\!>O+C_7H_5O_4(OH)+H_2O$$
$$=\begin{matrix}C_7H_5O_4\\C_7H_5O_4\end{matrix}\!\!>O+H_3AsO_4$$

The following constitution was first assigned by Schiff to his digallic acid:

$$COOH(OH)_2C_6H_2{\cdot}O{\cdot}C_6H_2(OH)_2COOH$$

and indeed by means of acetic anhydride only a tetra-acetyl compound was apparently produced. Later (*l.c.* 1873), a study of acetyltannin which was obtained as warty nodules, m.p. 137° (Trimble, The Tannins, I. 87), gives m.p. 139°; Nierenstein (Collegium, 1905, 23), 129°–131°; Dekker (Ber. 1906, 39, 2497), 129°; and Nierenstein (*ibid.* 1907, 40, 917), 146° (*cf.* Böttinger, *ibid.* 1884, 17, 1478), indicated that this possessed the formula $C_{14}H_5O_9Ac_5$, and the constitution given below was therefore adopted—

$$COOH(OH)_2{\cdot}C_6H_2{\cdot}O{\cdot}CO{\cdot}C_6H_2(OH)_3.$$

A penta-acetyl derivative was also given by digallic acid prepared both by the phosphorus oxychloride and arsenic methods (Ber. 1873, 68, 72), and there appeared at the time to be no doubt that this artificial product was identical with the natural tannin. Phosphorus pentachloride and phosphorus trichloride again produced digallic acid from gallic acid. According to Geschwender (Inaugural Diss. Munich, 1906), penta-acetyldigallic acid can be obtained in a crystalline condition from dilute alcohol.

By heating protocatechuic acid with arsenic acid, Schiff (Ber. 1882, 15, 2589) obtained his *diprotocatechuic acid* in the form of a hygroscopic glassy mass. This possessed the characteristics of a tannin and with boiling dilute mineral acids was converted into protocatechuic acid.

Dipyrogallol carboxylic acid from pyrogallol carboxylic acid and phloroglucinol tannic acid from phloroglucinol carboxylic acid were also prepared (Annalen 295, 40). Freda (Ber. 11, 2033; 12, 1576) did not obtain digallic acid by the interaction of gallic and arsenic acids, but only an arsenic compound, which on treatment with sulphuretted hydrogen gave gallic acid.

Biginelli (Gazz. chim. ital. 1909, 39 ii. 68) obtained from arsenic and gallic acid *arsenic gallic acid* $AsO(OH)_2O{\cdot}C_6H_2(OH)_2COOH$, *arsenic digallic acid*

$$(OH)AsO[O{\cdot}C_6H_2(OH)_2COOH]_2$$

and *dihexahydroxybenzophenone arsenic acid*

$$(OH)AsO[O{\cdot}C_6H_2(OH)_2CO{\cdot}C_6H_2(OH)_3]_2.$$

The second of these compounds, Biginelli suggests, forms one of the constituents of Schiff's artificial tannin.

Similar compounds are produced by the action of phosphoryl chloride or antimonic acid on gallic acid (Biginelli, *ibid.* 283) to which the following formulæ have been assigned:

$$PO(O{\cdot}C_6H_2(OH)_2COOH)_3,$$
$$SbO(OH)_2O{\cdot}C_6H_2(OH)_2COOH,$$
and $$(OH)SbO(O{\cdot}C_6H_2(OH)_2COOH)_2.$$

All these substances react as tannins, and it seems possible that Schiff's digallic acid preparations are in reality similarly constituted. On the other hand, Walden (Ber. 1898, 81, 3168) prepared Schiff's digallic acid by the arsenic acid method, and although he noted the difficulty of completely removing arsenic, this appeared to be absent from the purified compound (*cf.* also Nierenstein, Chemie der Gerbstoffe, Stuttgardt, 1910, 44).

By heating gallotannin with benzoyl chloride, Böttinger (Ber. 1889, 22, 2707) prepared a *benzoyltannin* in the form of a sandy light yellow coloured powder. Sisley (*l.c.*) and Dekker (*l.c.*) describe similar products. Vournasos (Le tannin de la noix de galle, 27), on the other hand, describes *pentabenzoylgallotannin* as a well-defined crystalline compound.

By heating a mixture of ethyl gallate and pyruvic acid with sulphuric acid, Böttinger (Ber. 1884, 17, 1476), prepared a substance $C_{14}H_{10}O_9,2H_2O$, which he at first regarded as digallic acid. It consisted of a very hygroscopic mass which had the properties of a tannin, gave a penta-acetyl compound, and with lead acetate solution yielded a dull yellow precipitate. As, however, by digestion with boiling dilute hydrochloric acid no gallic acid was produced, it could only be an isomeride of natural gallotannin.

According to Hunt (Chem. News, 52, 49), a substance which behaves in many respects like tannin can be prepared by the interaction of monobromoprotocatechuic acid and potassium gallate

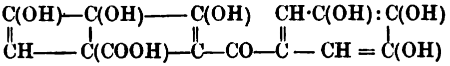
$$C_6H_2(OH)_3COOK + C_6H_2Br(OH)_2COOH$$
$$= C_6H_2(OH)_3CO{\cdot}O{\cdot}C_6H_2(OH)_2COOH + KBr.$$

but Schiff (Gazz. chim. ital. 1897, 21, i. 90) was unable to synthesise tannin by this method.

Herzig and Tscherne (Ber. 1905, 38, 989) obtained *methyltannin* by the action of diazomethane on gallotannin suspended in ether, and describe it as a colourless amorphous powder, m.p. 124°–126°. It had the composition $C_{24}H_8O_7(OCH_3)_8$ or $C_{24}H_{10}O_7(OCH_3)_5$, is dextrorotatory and when hydrolysed gives a mixture of *trimethylgallic acid* and 3 : 4-*dimethylgallic acid*. The percentage of methoxyl found, however, approximates to that required for a pentamethylgallotannin (Herzig, *ibid.* 1908, 41, 83). Later, Herzig and Renner (Monatsh. 1909, 30, 543) consider that their methyltannin may possibly be a mixture of substances which have approximately the same composition, and indeed contain pentamethoxy derivatives of the tannin constituents described by Nierenstein (see below). Rosenheim (Chem. Soc. Proc. 1905, 21, 157), by means of methyl sulphate, obtained a compound having the composition of a tannin pentamethyl ether.

Whereas, for a considerable time, Schiff's formula was generally recognised as the best known expression for the constitution of gallotannin, it had been pointed out by Scheibler in 1866 (Zeitsch. Zuckerind. 16, 33), by van Teigheim in 1867 (Ann. Sci. Nat. [v.] 8, 210) and by Gunther in 1872 (Ber. pharm. Ges. 5, 172) that natural gallotannin was optically active.

Owing no doubt to the idea that unless carefully purified, gallotannin obstinately retains traces of sugar, this fact did not attract special attention until Schiff (Gazz. chim. ital. 1895, 25, ii. 437) noted that the pure substance possesses a dextro-rotation ($[\alpha]_D = +14°$ to $+67°$). In order to provide for the assymetric carbon atom, a modification of his earlier formula was accordingly necessary, and he now suggested that gallotannin should be represented as a ketonic compound of the following constitution:



$$\begin{array}{llllll} C(OH)- & C(OH)- & C(OH) & & CH{\cdot}C(OH):C(OH) & \\ \| & | & \| & & \| \qquad\qquad | & \\ CH- & C(COOH)- & C- & CO- & C - CH = C(OH) & \end{array}$$

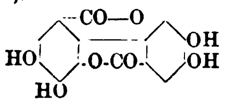
On the other hand, by the action of phenylhydrazine under varied conditions, no hydrazone could be prepared from gallotannin.

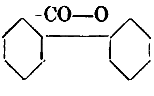
According to Walden (Ber. 1897, 30, 3151), who examined the purest samples of commercial tannin available, these products, as already indicated by Schiff, vary considerably in optical activity, having $[\alpha]_D$ from $+15°$ to $+67°$, and are evidently mixtures.

Whereas Paterno (Zeitsch. physikal. Chem. 1899, 4, 458) found the molecular weight of tannin in water to be 2643–3700, and that of Schiff's digallic acid 660, Sabanéeff (J. Russ. Phys. Chem. Soc. 1890, 22, 104) showed that in acetic acid gallotannin gave the figure 1322. Krafft, again (Ber. 1899, 32, 1613), found for gallotannin in water 1587–1626.

Walden (Ber. 1899, 31, 3167), on the other hand, showed that the molecular weight indicated by Schiff's digallic acid in boiling acetone is about 316, whilst samples of Merck's and Schuchardt's tannin in the same solvent respectively gave figures of 753–763, and 1350–1360. Again, the affinity coefficient of Schiff's digallic acid is K=0·0012, whereas that of tannin, which varies greatly with the concentration, is from K =0·0001 to K=0·00006. Spectrometric examination of solutions of gallotannin and digallic acid showed also that their absorption powers for all regions of the spectrum are entirely different, and from these facts there could be no doubt that gallotannin and Schiff's digallic acid are distinct compounds. Moreover, it was not possible to regard digallic acid as the inactive modification of gallotannin. Rosenheim and Schidrowitz (Chem. Soc. Trans. 1898, 73, 878), who examined samples of commercially 'pure' gallotannins, again pointed out the wide limits through which the rotation of these varied, the minimum being $[\alpha]_D+11°$ and the maximum $+74·2°$. The important point was also indicated that these commercial products could be separated into fractions the rotatory powers of which varied from $[\alpha]_D\pm0°$ to $[\alpha]_D+75·2°$, and it was further concluded that in each of the original samples a homogeneous gallotannin exists, possessing an optical activity of about $[\alpha]_D+75°$. As a confirmation of this point it was noted that the quinine salts and penta-acetyl compounds prepared from gallotannins of $[\alpha]_D+11°$, up to $[\alpha]_D+75°$ were identical in rotatory power *inter se* with those prepared from the purified gallotannin.

According to Nierenstein (Ber. 1905, 38, 3641) when gallotannin is distilled with zinc dust, diphenylmethane is produced, a result which is in harmony with Schiff's formula for digallic acid, in that it has been previously found that ellagic acid (1), and diphenylmethylolid (2) (Graebe, *ibid.* 1903, 36, 212) by a similar method give fluorene (3) (*cf.* also Perkin and Nierenstein, Chem. Soc. Trans. 1905, 87, 1412).

(1)


(2)


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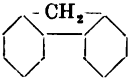
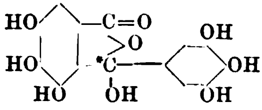


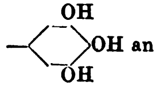
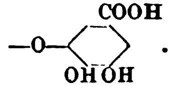
Dekker (Ber. 1906, 39, 2497; *ibid.* 3784) suggested that gallotannin should be represented as a derivative of phthalic anhydride.



and it was considered that this formula is in harmony with the optical activity, almost complete hydrolysis to gallic acid and the formation of diphenylmethane. According to numerous workers, however, gallotannin gives only a penta-acetyl derivative, whereas such a constitution indicates seven hydroxyl groups, and though Dekker describes a hexa-acetyl tannin $[\alpha]_D+64·4°$ the existence of this is doubtful.

Dekker (De Looistoffen, 1908, ii. 30, 1908) was unable to confirm the production of diphenylmethane from tannin as observed by Nierenstein (*l.c.*), and obtained in this manner diphenyl. Nierenstein (Chemie der Gerbstoffe, 1910, 47), however, maintains the correctness of his former work.

Lloyd (Chem. News, 1908, 97, 133) concludes that gallotannin contains three digallic groups united to each other to form a six-membered ring of the type $CXY{<}{O\cdot CXY \atop O\cdot CXY}{>}O$ in which

X=  and Y=  .

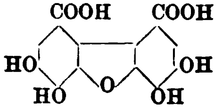
Nierenstein (Ber. 1907, 40, 916) separates acetyl gallotannin which, on analysis, behaves as a penta-acetyl compound, into two amorphous components (*a*), m.p. 203°–206°, present in small quantity, and (*b*) the main product, m.p. 166°. The former when hydrolysed gives gallic acid, and on oxidation by means of potassium persulphate and acetic acid, ellagic acid. By means of zinc dust, the penta-acetyl tannin, m.p. 203° (Ber. 1908, 41, 77), may be reduced to the acetyl derivative, m.p. 166°. Again the compound, m.p. 166°, which is termed *acetyl-leucotannin*, is not a fully acetylated compound, but on further treatment gives hexa-acetyl-leucotannin, m.p. 159°. Thus gallotannin is considered to be a mixture of digallic acid and leucotannin

$$C_6H_2(OH)_3CH(OH)O{\cdot}C_6H_2(OH)_2COOH$$

the latter being evidently the main component of the mixture.

Penta-acetyl-leucotannin (Ber. 1909, 42, 1122) is hydrolysed by boiling dilute sulphuric acid with formation of *gallic aldehyde* and *gallic acid* as its formula suggests, and when oxidised with persulphate and sulphuric acid in boiling acetic acid gives in addition to ellagic acid, a red amorphous product *purpuro-tannin* (C =69·14, H=2·84) which on distillation with zinc dust yields naphthalene.

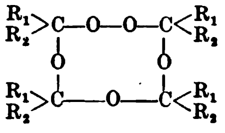
In a later paper (Nierenstein, Annalen, 1912, 386, 318) the formula $C_{14}H_8O_9$ (C=52·5; H=2·5 is assigned to this compound, and the *quinolin* salt $C_{14}H_8O_9{\cdot}2C_9H_7N$ *tetra-acetyl* compound, m.p. 324°–327°, *tetrabenzoyl* compound, m.p. 279°–281°, and *tetramethylether*, m.p. 242°–244°, are described. By distillation with zinc dust it gives *diphenylene* and not naphthalene, as was at first considered to be the case. With piperidine at 180° it gives 1:2:7:8 *tetrahydroxydiphenylene oxide* $C_{12}H_8O_5$, m.p. 334°–338°, with hydriodic acid and phosphorus *diphenylene oxide*, and from these results appears to possess the following constitution:



Iljin, who studied the action of zinc dust on a boiling 10 p.c. aqueous solution of tannin for 15 to 20 hours, obtained an amorphous substance which has $[\alpha]_D^{18·4}+24·1°$ in 95 p.c. alcohol, gives coloured precipitates with metallic salts, and gallic acid without gallic aldehyde when heated with 20 p.c. sulphuric acid in a current of hydrogen (J. pr. Chem. 1909, [ii.] 5, 80, 332).

According also to Herzig and Renner (Monatsh. 1909, 30, 543), tannin methyl ether (*l.c.*) is practically unaffected by boiling with acetic acid, zinc, sodium acetate and acetic anhydride, no leuco compound being thus produced.

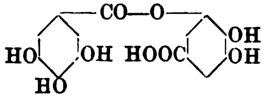
Iljin (J. Russ. Phys. Chem. Soc. 1908, 39, 470; Chemie der Gerbstoffe, 1910, 49) obtained two phenylhydrazine derivatives $C_{74}H_{58}N_6O_{30}$ and $C_{98}H_{82}N_{14}O_{26}$ from gallotannin. He suggests for gallotannin the formula $C_{56}H_{40}O_{33}$, and proposes the following constitution, in which $R_1 = -CO{\cdot}C_6H_2(OH)_3$ and $R_2 = -C_6H_2(OH)_3$:

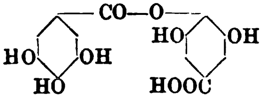


E. Fischer (Ber. 1908, 41, 2875), by coupling tricarbomethoxygallyl chloride with dicarbomethoxygallic acid, obtained a product which, on hydrolysis, gave a substance, m.p. 275°–280°, crystallising in prisms or needles. This was considered to be possibly a mixture of digallic acid with gallic acid, but was subsequently shown (1911, see below) to be a slightly impure *digallic acid*

$$(OH)_3C_6H_2{\cdot}CO{\cdot}O{\cdot}C_6H_2(OH)_2COOH.$$

According to Nierenstein (Ber. 1910, 43, 628), by converting gallotannin into the carboethoxy derivative, hydrolysing this with pyridine and repeating the operation three or four times, there is obtained a digallic acid $C_{14}H_{10}O_9,2H_2O$ crystallising in small needles from alcohol and water (1 : 3) which sinters at 214° and melts at 268°–270°. It (1) is optically inactive, when hydrolysed gives gallic acid, and on oxidation with hydrogen peroxide ellagic acid, but is not identical with Fischer's digallic acid (2) which does not yield ellagic acid. Nierenstein formulates these compounds as follows:

(1) 

(2) 

Penta-acetyldigallic acid needles, m.p. 211°–214°, *pentabenzoyldigallic acid* needles, m.p. 187°–189°, *pentacarbethoxydigallic acid*, small cubes, m.p. 194°–195°, and *sodium digallate* are described.

By digestion with boiling acetic anhydride and zinc dust, penta-acetyldigallic acid gives dl-*hexa-acetyl-leucotannin*, m.p. 154°–155°, cubes, and may be separated by means of the strychnine salt into l-*hexa-acetyl-leucotannin*, having m.p. 151° and $[\alpha]_D^{15} - 4{\cdot}6$, and *d-hexa-acetyl-leucotannin*, having m.p. 153°–154° and $[\alpha]_D^{20} + 121{\cdot}5°$.

Iljin (J. pr. Chem. 1910, [ii.] 82, 422) redetermined the molecular weight of specially purified gallotannin in acetone, and found values of 1247–1637, confirming the results of Sabanéeff and of Walden (*l.c.*). Accordingly he considers that gallotannin must consist largely of a complex derivative of gallic acid, distinct from the digallic acid and leucotannin of Nierenstein.

When gallotannin is boiled for 4 hours with zinc oxide the filtrate does not react with ferric chloride. The residue decomposed with sulphuric acid gives gallic acid and the compound previously obtained by the action of zinc dust on tannin (*l.c.*) in approximately equal amount (Iljin, *ibid.* 1910, [ii.] 81, 327). Manning (J. Amer. Chem. Soc. 1910, 32, 1312) prepares *ethyl gallotannate* $C_{51}H_{52}O_{28}, 5H_2O$ yellow crystals, m.p. 157°, by passing dry hydrogen chloride into an alcoholic solution of gallotannin; this on hydrolysis gives ethyl alcohol, dextrose and gallic acid. This compound may be synthesised by treating a mixture of ethyl gallate and dextrose with phosphoryl chloride.

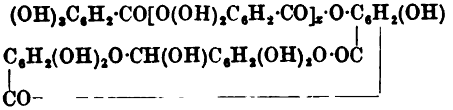
Fischer and Freudenberg (Annalen, 1911, 384, 225) coupled dicarbomethoxygallic acid and tricarbomethoxygallyl chloride in alkaline solution, and by hydrolysis of the resulting product, obtained a pure *digallic acid*. It crystallises in needles, is much less sparingly soluble in water than gallic acid (approximately 12 times), and melts at 275° (corr. 282°) with decomposition. With ferric chloride it gives a blue-black coloration and possesses the properties of a tannin. For a description of the diprotocatechuic acid, digentisic acid and di-β-resorcylic acid, of these authors, see below.

Paniker and Stiasny (Chem. Soc. Trans. 1911, 99, 1819), who consider that the chemical constitution of gallotannic acid is not definitely settled, investigated the acid character of this substance by the diazo-acetic ester method of Fraenkel (Zeitsch. physikal. Chem. 1907, 60, 202), because, according to the previously expressed view of Böttinger (Ber. 1884, 17, 1503), Dekker (*ibid.* 1906, 39, 2497), and Walden (*ibid.* 1898, 31, 3170), no free carboxyl group is present in this compound. It is shown that gallotannin is to be regarded as an acid, the affinity constant being of a distinctly higher order than that shown by phenols.

Gallotannin can be divided into two parts by saturating its solution with sodium bicarbonate, one part being soluble in ethyl acetate, whilst the other forms a sodium salt. Thus the former product is shown to be only half as acid as that which is set free on acidifying the sodium salt in solution. The experiments favoured the view of Kunz-Krause (Schweiz. Wochensch. Chem. Pharm. 1898, No. 38), Walden (*l.c.*), Aweng (Rev. Int. Falsif. 1898, 11, 29), and Nierenstein (*l.c.*), that gallotannin is a mixture of two or more chemical individuals.

With alcoholic potassium acetate, gallotannin gives a precipitate of the potassium salt which appears to have the unimolecular formula $C_{14}H_9O_9K$. This compound is devoid of optical activity.

According to Nierenstein (Annalen, 1912, 388, 223), when an aqueous solution of tannin is reduced with zinc dust by Iljin's method (*l.c.*), dl-*leucodigallic acid*, fine needles, m.p. 278°–280°, is produced, and the same compound can also be prepared by the reduction of digallic acid. By means of the carbethoxy derivative, this can be resolved into l-*leucodigallic acid*, m.p. 276°–277°, which has $[\alpha]_D^{15} -70\cdot26°$, and d-*leucodigallic acid*, m.p. 276°–277°, which has $[\alpha]_D^{19} +104\cdot2°$ in water. As leucodigallic acid does not possess tanning property, it cannot be present in gallotannin, and the author now therefore discards his theory that the latter is composed of a mixture of digallic and leucodigallic acids. Tannins are accordingly now considered to consist of *polydigallyl-leuco-digallic anhydrides*



$$\begin{array}{l} (OH)_3C_6H_2\cdot CO[O(OH)_2C_6H_2\cdot CO]_x\cdot O\cdot C_6H_2(OH) \\ C_6H_2(OH)_2O\cdot CH(OH)C_6H_2(OH)_2O\cdot OC \\ CO- \end{array}$$

Schering's tannin, employed by the author, gives digallic and leuco-digallic acids in the proportions 3 : 1 or 4 : 1 (compare Ber. 1907, 40, 916), and is consequently a digalloyl, tri- or tetraleucodigallic anhydride. For further details, the original paper must be consulted.

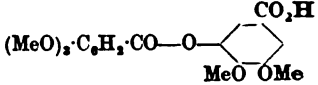
E. Fischer and Freudenberg (Ber. 1912, 45, 915) take an entirely different view of the constitution of gallotannin, and announce the important fact, not generally suspected, that this compound contains a glucose nucleus. Purified preparations of gallotannin have $[\alpha]_D^{20}$ approximately +70°, and these samples, when hydrolysed with acid, yield gallic acid and a small amount of dextrose. Gallotannin is most probably a compound of dextrose with five molecules of digallic acid, of the nature of penta-acetyldextrose, and such a constitution will agree with its high molecular weight, optical activity, faint acidity and ready solubility in water. Synthetical tannin compounds, derivatives of dextrose, are described, the properties of which favour this suggestion. Tricarbomethoxygalloyl chloride in chloroform solution reacts with dextrose in the presence of quinoline, to form penta-tricarbomethoxygallyl glucose, from which, by hydrolysis with alkali, *pentagalloyl glucose* is produced. It is a yellow powder of astringent taste, possesses the power of precipitating gelatin solutions, and has $[\alpha]_D +31°$ to +35° in water, or +44·4° in alcohol. Similar compounds of gallic acid with *a*-methylglucoside and glycerol, and of *p*-hydroxybenzoic acid with dextrose are also described.

Manning and Nierenstein (Ber. 1912, 45, 1546) consider that a sugar nucleus is not present in pure gallotannin, and point out that this is not produced when either Schering's tannin or Herzig and Renner's methyl tannin (*l.c.*) is hydrolysed with alkali. Again, ethyl gallate is the sole product of the esterification of this tannin.

Herzig (Ber. 1912, 45, 1985) considers that the argument of these authors is no proof of the absence of a sugar nucleus in methyl tannin or tannin itself, whereas Biddle and Kelley (J. Amer. Chem. Soc. 1912, 34, 918) show that the so-called ethyl tannate of Manning is in reality ethyl gallate. On the other hand, Feist reiterates the fact (Ber. 1912, 45, 1493) that in 1908 (Chem. Zentr. 1908, ii. 1352) he isolated glucogallic acid, a compound of gallic acid and glucose, from Turkish gall nuts.

Fischer and Freudenberg (Ber. 1912, 45, 2709) further support their view that gallotannin is a pentadigalloyl glucose, and in continuation of their syntheses of tannin compounds employ pentamethyl-*m*-digalloyl chloride with interesting results. Whereas the digallic acid previously synthesised by these authors is the *p* compound (Ber. 1910, 43, 628), gallotannin is derived from the *m*-acid, for Herzig has shown that methyl tannin, when hydrolysed, gives gallic acid trimethylether and 3 : 4 gallic acid dimethyl ether (*cf.* also Nierenstein).

When the trimethylether of galloyl chloride reacts with 3 : 4 gallic acid dimethyl ether, according to the method employed by these authors, *pentamethyl*-m-*digallic acid*



m.p. 192°–193°, is produced (*cf.* Mauthner, Ber. 1905, 38, 389; Monatsh. 1909, 30, 543), and from this the chloride, m.p. 109°–110°, is readily obtained. In the presence of quinoline, this is condensed with *a*- and *β*-glucose respectively, and such a procedure was adopted, because it was found that benzoyl and cinnamyl chlorides, in a similar manner, give with *a*- and *β*-glucose stereoisomeric compounds.

The *m*-digalloyl derivatives thus prepared are amorphous, possess the composition of penta-[pentamethyl-digallyl]-glucose, but appear in each case to be a mixture of stereo-isomerides Thus the *a*-glucose product in acetylene tetrachloride had $[\alpha]_D +28°$ (approx.), and after repeated solution in hot alcohol $[\alpha]_D +14°$ (approx.), whereas the *β*-glucose compound $[\alpha]_D +19\cdot5°$ behaved similarly.

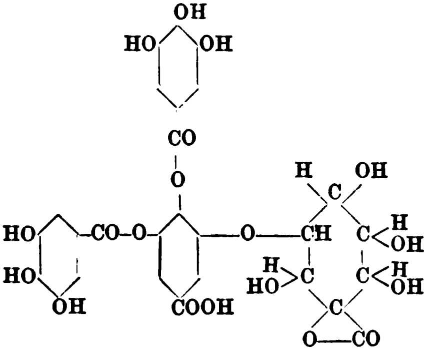
In case gallotannin is penta-*m*-digalloyl glucose it is evident that this product will represent its methyl ether, and indeed a very close resemblance appears to exist between this substance and the preparation of Herzig. The methyl ether prepared from natural tannin (Herzig, *l.c.*) is not a uniform substance, but probably also a mixture of stereo-isomerides, the sample employed having in acetylene tetrachloride $[\alpha]_D^{26} +14°$, and after repeated solution in acetone and methyl alcohol $[\alpha]_D^{21} +10\cdot6°$. Finally, the criticisms of Manning and Nierenstein (*l.c.*) as to the absence of glucose in pure tannin are shown to be valueless. It is likely that the work of Fischer and Freudenberg may soon culminate in the synthesis of penta-*m*-digalloyl glucose itself, in which case it is to be hoped that the mystery which has so long enshrouded the constitution of this important compound will be finally dispersed. On the other hand, the elaborate results of Nierenstein on such a basis are at present difficult to comprehend.

For further references to *Gallotannin* see Harnack (Arch. Pharm. 1896, 234, 537), colour reaction; Ljubavin (J. Russ. Phys. Chem. Soc. 1901, 33, 680), tannin and tartar emetic; Thibault (Bull. Soc. chim. 1903, (iii.) 29, 745), tannin and bismuth; Vigneron (J. Pharm. Chim. 1906, [vi.] 23, 469), iodotannin; Farbewerke vorm. Meister, Lucius and Brüning (D. R. P. 173729), mixed anhydrides of tannic and cinnamic acids; Biginelli (Gazz. chim. ital. 1907, 37, ii. 205; *ibid.* 1903, 38, i. 559), tannates of quinine; Hildebrandt (D. R. P. 188318), tannin and formaldehyde; Francis and Nierenstein (Collegium, 1911, 335), action of benzoyl chloride and potassium cyanide on benzoylhydroxybenzoic acids and on acylated hydroxybenzoylhydroxybenzoic acids; Nierenstein (Die Gerbstoffe).

Chestnut tannin. Chestnut tannin has been examined by Nass (Inaugural Diss. 1884, Dorpat, Russia) and by Trimble (The Tannins, ii. 119). According to the latter author it is probably identical with ordinary gallotannin (*see* CHESTNUT EXTRACT).

Chebulinic acid or Eutannin. This tannin was isolated by Fridolin from myrabolans, *Terminalia Chebula* (Retz.), which also contain an ellagitannin. It crystallises in rhombic prisms, is sparingly soluble in cold water, gives with ferric chloride a blue-black precipitate and by heating with water is converted into gallic acid and a new tannin.

Thoms (Chem. Zentr. 1906, i. 1829; Apotheker Zeit. 1906, 21, 354) has found that commercial *eutannin* is identical with chebulic acid $C_{28}H_{22}O_{19}$. It consists of small colourless needles, containing water of crystallisation, reacts acid to litmus paper, decomposes at 234°, and has $[\alpha]_D$ initially $+61·7°$, gradually rising to $+66·9°$. An *ennea-acetyl* and *methyl* derivative are described, the latter giving trimethylgallic acid by the action of sodium hydroxide solution. With water at 100°–150° the tannin yields gallic acid and *eutannin hydrate* $C_{28}H_{24}O_{20}$, a colourless powder decomposing at 200°–210°. When eutannin is dissolved in cold sodium hydroxide, the solution acidified with acetic acid, and then treated with lead acetate solution, the resulting precipitate, after decomposition with sulphuretted hydrogen, gives gallic acid, and a tannin $C_{14}H_{16}O_{12}$ or $C_{14}H_{14}O_{11}$, which consists of a yellow powder, having $[\alpha]_D +26°$ at 15°, and giving a blue coloration with ferric chloride. To chebulinic acid the following constitution is assigned:



According to Fischer and Freudenberg (Ber. 1912, 45, 915), when hydrolysed chebulinic acid gives dextrose.

Hamamelitannin. This compound, one of the few gallotannins to be isolated in a crystalline condition, occurs in the bark of the *Hamamelis virginiana* (Linn.), a tree, 10 to 12 ft. high, common in North America. The bark, previously extracted with light petroleum to remove plant wax, is exhausted with ether-alcohol (5 : 1), the solution evaporated, the residue dissolved in a little alcohol and treated with ether to precipitate certain impurities. Evaporation of the ethereal liquid gives a product, a hot aqueous solution of which, after treatment with alumina and animal charcoal, deposits, on cooling, the substance in the form of small colourless needles. From a dilute aqueous solution, hamamelitannin

$$C_{14}H_{14}O_9$$

crystallises with $5H_2O$, but deposited from strong solutions the crystals contain $2\frac{1}{2}H_2O$. The air-dried substance melts at 115°–117°, although when dried at 100° the melting-point is 203°. Hydrolysed with boiling dilute sulphuric acid, gallic acid only was produced, and the presence of a sugar could not be detected. Hamamelitannin is dextrorotatory $[\alpha]_D=+35·43°$. According to Fischer and Freudenberg (Ber. 1912, 46, 2712), however, this tannin can contain a sugar nucleus.

Benzoylhamamelitannin $C_{14}H_9O_9(C_7H_5O)_5$ is a yellow powder which melts at about 125°–132° (Grüthner, Arch. Pharm. 236, 303).

Oak wood tannin is probably a member of this group, but is described under the heading of *Phlobatannins*.

Sumach tannin (*see* SUMACH).

Diprotocatechuic acid is prepared by coupling monocarbomethoxyprotocatechuic acid with dicarbomethoxyprotocatechuyl chloride in alkaline solution and subsequently hydrolysing the product. It possesses the constitution

$$(OH)_2C_6H_3·CO·O·C_6H_3(OH)COOH,$$

and consists of fine needles which begin to sinter at 230° and melt with decomposition at 237°–239°. It is much more sparingly soluble in water than protocatechuic acid, gives with ferric chloride a bluish-green coloration and possesses tanning properties (Fischer and Freudenberg, Annalen, 1911, 384, 2, 238).

Di-β-resorcylic acid prepared from β-resorcylic acid by the same general method

$$(OH)_2C_6H_3·CO·O·C_6H_3(OH)COOH,$$

forms small microscopic needles, melting at 215° (corr.), sparingly soluble in water. It gives with ferric chloride a violet-red coloration and behaves as a tannin.

Digentisic acid

$$(OH)_2C_6H_3·CO·O·C_6H_3(OH)COOH$$

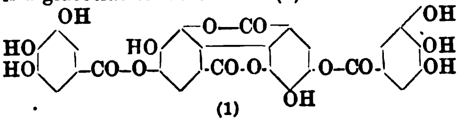
crystallises in fine needles, m.p. 208°–209° (corr.), sparingly soluble in water. The aqueous solution precipitates gelatin and gives a blue coloration with ferric chloride.

Fischer and Hoesch (*l.c.* 224) and Fischer and Lepsius (*l.c.* 224) have prepared numerous other acids of this type, but it is not stated as yet if these are to be regarded as tannins. Lecanoric acid, ramalic acid, evernic acid and no doubt other lichen acids which structurally belong to this group may be found also to possess tanning property.

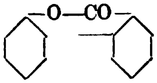
GROUP II.—DIPHENYLMETHYLOLID OR ELLAGITANNINS.

This tannin group, which has for its mother substance diphenylmethylolid (2), is at present only represented by one well authenticated member known as ellagitannin, unless indeed pomegranate tannin (*see* below) is a distinct compound. Whereas Perkin and Nierenstein

(Chem. Soc. Trans. 1905, 87, 1428) considered that ellagitannin was probably formed by the condensation of two molecules of digallic acid and possessed the formula (1) or was a glucoside of this substance, according to Nierenstein, ellagitannin (*q.v.*) (*cf.* also Ber. 1912, 45, 365) is a glucoside of luteoic acid (2).



(1)



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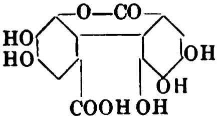


(3)

Numerous natural tannin matters yield ellagic acid, but these have been little investigated, and it is likely that glucosides forming ellagic acid but differing from ellagitannin itself in the character of their sugar nuclei will be discovered.

Though various hydroxydiphenylmethylolid compounds have been synthetically prepared, *e.g.* metellagic acid $C_{15}H_5O_4(OH)$, catellagic acid $C_{14}H_4O_4(OH)_2$, flavellagic acid $C_{14}HO_4(OH)_5$ and cæruleoellagic (cyanellagic) acid $C_{14}O_4(OH)_6$, ellagic acid is the only member of this group which has been isolated from natural sources.

Pomegranate tannin $C_{20}H_{16}O_{13}$ is an amorphous greenish-yellow substance contained in the root bark of *Punica Granatum* (Linn.). Boiling dilute sulphuric acid hydrolyses it with formation of a sugar and ellagic acid (Rembold, Annalen, 143, 385).

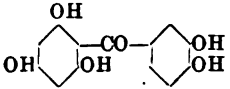
GROUP III.—CATECHOL OR PHLOBATANNINS.

The catechol tannins are characterised among other distinctive features by the important fact that when digested with boiling dilute mineral acids a red precipitate known as 'anhydride' or 'phlobaphane' is produced. The designation 'catechol,' arises from the fact that the majority of these substances give a green coloration with ferric chloride, and protocatechuic acid or catechol as one of their decomposition products. Such a classification is, however, misleading, in that by comparison with gallotannin, one is led to infer that these substances are similarly constituted and derived from diprotocatechuic acid only

$$(OH)_2C_6H_3\cdot CO\cdot O\cdot C_6H_3(OH)COOH.$$

When hydrolysed, however, diprotocatechuic acid gives two molecules of protocatechuic acid without production of phlobaphane (Emil Fischer, private communication). Moreover certain phlobaphane-yielding compounds are now known to exist in which a catechol nucleus is absent. Thus the cyanomaclurin of Jakwood (*q.v.*) is an instance in point, for although it contains only phloroglucinol and resorcinol nuclei, it readily yields a red anhydride of this character (*cf.* also Mimosa tannin, Pistachia tannin and Maletto · tannin). Evidently therefore the phlobaphane reaction is either due to the special structure of the tannin itself, or to the presence of a second phenolic grouping other than catechol in the molecule. This structure may perhaps vary in certain cases, but until this is clear it appears to be preferable to include all phlobatannins under one group rather than to complicate the subject by the introduction of subdivisions.

Böttinger and Etti (*l.c.*) have suggested a benzophenone structure for certain tannins, and this applied to the phlobatannins has, at first sight, the merit that *maclurin* (*see* OLD FUSTIC)



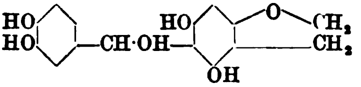
with dilute hydrochloric acid gives rufimoric acid (Wagner, Jahres. 1851, 420), a red amorphous phlobaphane-like mass. ***Kinoin*** (*see* Kino), usually regarded as the methyl ether of a pentahydroxy-benzophenone, is readily transformed into kino-red, whereas ***aromadendrin*** (*see* Kino), apparently also a benzophenone derivative, and probably a maclurin monomethyl ether, resembles, according to Maiden and Smith, ***catechin*** in many of its properties. It has not yet been ascertained if the carboxylic acids of certain hydroxybenzophenones are tannins, but on the other hand it is to be remembered that compounds possessing such a structure will be strong mordant dyestuffs, a property which is generally absent from tannins of the so-called catechol type. As already indicated, many phlobatannins are known which contain two distinct nuclei, more frequently phloroglucinol in addition to catechol, a fact which in these cases accounts for their reactivity with diazobenzene. More difficult to understand, however, is the precipitation of all phlobatannins in aqueous solution with bromine; this could be accounted for in those instances in which phloroglucinol or resorcinol nuclei are present in the compound, but curiously enough no difference in this respect appears to have been observed in cases where evidence as to the existence of these latter groupings has been of a negative character. Though by incautious alkali fusion, the existing phloroglucinol nucleus may escape detection and probably in many instances has done so, this evidence is such that it is hard to presume that in all cases bromine precipitation arises from the presence in these compounds of a specific phenolic grouping.

It is most probable that the phlobaphane reaction is, in many cases, to be assigned to the well-known reactivity of the phloroglucinol group present in these substances, and this has also been suggested by Emil Fischer. Thus coloured compounds can be obtained by the interaction of phloroglucinol with many aldehydes of which the red phloroglucinol vanillein is an example, and moreover the phloroglucides of Counder (Ber. 1895, 28, 26), prepared by passing hydrogen chloride into mixtures of phloroglucinol and various sugars in aqueous solution are coloured, the *d*-galactose phloroglucide possessing a red tint. Again, by boiling dextrose and phloroglucinol with dilute hydrochloric acid, a brownish-red precipitate of a phlobaphane-like character can be easily produced (private communication). Interesting in this respect also is the 'phlorotannin red' of Schiff (Annalen, 245, 40), which he obtained by heating his so-called diphloroglucinol carboxylic acid to 160°–175°.

That phlobatannins like gallotannin owe their tanning property, as a rule, to the depside grouping appears likely, and it has been observed by Trimble (The Tannins, II. 91) that tannins from various species of oak, on long digestion with boiling 2 p.c. hydrochloric acid, give not only phlobaphane but some quantity of protocatechuic acid.

In the light of the researches of E. Fischer and Freudenberg (*l.c.*), it is also to be anticipated that many of these compounds will be eventually found to possess a sugar nucleus.

Closely connected with the phlobatannin group are the well-defined crystalline substances catechin, aca-catechin and cyanomaclurin, to the first of which the constitution



has been assigned by v. Kostanecki and Lampe.

Catechin, although not a tannin, reacts with pine wood and hydrochloric acid, gives with bromine water the insoluble bromcatechuretin and readily yields substances of the phlobaphane character. Though the evidence is not precise it is stated by Loewe and also by Etti that catechin can be readily transformed into catechutannic acid, a substance existing side by side with it in the plant and possessing properties typical of the phlobatannin group. This change from catechin to catechutannic acid occurs, it is suggested, by mere abstraction of water, presumably between two molecules, and in any case it is difficult to understand how, by the simple processes employed, a depside grouping could be here produced. If, therefore, the statement of these authors is correct, some explanation other than those suggested above is required to express the tanning properties of this compound, and indeed there is no absolute reason to presume the depside grouping to be essential in this respect. It has indeed been surmised that the catechol tannins of numerous plants owe their origin to the prior existence of substances of the catechin type, and that in addition to the compounds previously enumerated, the so-called quebracho resin and guarana catechin are intermediate products of tannin formation. Again, according to Procter (private communication), a colourless catechin-like substance is to be found in mangrove cutch.

With the exception of coca-tannic acid, no crystalline catechol tannins have been described, but all are amorphous and very similar in appearance to natural gallotannin, although on keeping, especially in the moist condition, they are apt to develop a red tint. According to Perkin, most phlobatannins can be prepared in a nearly colourless condition by extracting a solution of the crude tannin to which sodium bicarbonate has been added with ethyl acetate (*cf. Gallotannin*).

Numerous phlobatannins have been isolated, and a description of them is given below, although it is extremely doubtful whether the majority of these are individuals. In many cases, indeed, the general reactions of these compounds are the same, and considering the extreme difficulty in the effective purification of amorphous preparations of this character, specific differences which have been observed will no doubt, on further investigation, largely disappear. Trimble (*l.c.* ii. 132), who submitted certain phlobatannins to careful purification, found that there was a fair approximation in their percentage compositions, and it is thus natural to presume that the known members of this group are not so numerous as was formerly considered to be the case.

Anachueta wood and bark contain a tannin which gives a green coloration with iron salts.

Aspertannic acid $C_{14}H_{16}O_8$ was obtained by Schwarz from Woodruff (*Asperula odorata* [Linn.]), and gives a green colour with ferric salts. It does not yield precipitates with albumen, gelatin, and tartar emetic solutions.

Atherospermatannin from the bark of *Atherosperma moschatum* (Labill.), gives a green colour with ferric salts. A lead salt $C_{10}H_{14}PbO_9$ has been described by Zeyer (Jahrb. Min. 1861, 769).

Barbitamao tannic acid from the bark of the *Stryphnodendron Barbatimum* (Mart.) (Wilbuszwitcz, Ber. Ref. 1886, 19, 349), is an amorphous red powder, which yields a phlobaphane and, on fusion with alkali, *protocatechuic acid* and *phloroglucinol*.

Beech tannin from the bark of the red beech contains a tannin of the composition $C_{20}H_{22}O_9$ (Etti, Monatsh. 10, 650).

Caffetannic acid $C_{15}H_{18}O_9$ occurs in coffee berries in the form of calcium and magnesium salts (Rochleder, Annalen, 59, 300); in cainia root *Chiococca brachiata* (Ruiz. et Pav.) (Rochleder and Hlasiwetz, *ibid.* 1848, 66, 35); *Nux vomica* (Sander, Arch. Pharm. 1897, 235, 133); St. Ignatius beans (*ibid.*) and Paraguay tea, *Ilex paraguensis* (A. St. Hill.) (Rochleder, Annalen, 1847, 66, 39) (*cp.* also Graham, Stenhouse and Campbell, J. pr. Chem. 1856, 69, 815; Arata, Ber. 1881, 14, 2251; Kunz-Krause, Arch. Pharm. 1893, 231, 613; Ber. 1897, 30, 1617).

It is an amorphous powder readily soluble in water, gives a dark green coloration with ferric chloride, and when boiled with potassium hydroxide solution gives *caffeic acid* and a sugar (Hlasiwetz, Annalen, 1866, 142, 220), which is glucose (Sander, *l.c.*). On dry distillation *catechol* is formed, and by fusion with alkali *protocatechuic acid* is obtained. The ammoniacal solution becomes green on exposure to air with formation of viridic acid, a substance which is also present in coffee berries in the form of its calcium salt (Rochleder, Annalen, 63, 197). According to Griebel (Inaugural Diss. Munich, 1903) caffetannic acid is $C_{13}H_{24}O_{10}$, and a penta-acetyl derivative corresponding to this formula is described.

Callutannic acid $C_{14}H_{14}O_9$ contained in heather, *Calluna vulgaris* (Salisb.), is an amber coloured substance. It gives a green coloration with ferric chloride and when heated with dilute mineral acids yields an amorphous anhydro derivative $C_{14}H_{10}O_7$ (Rochleder, Annalen, 84, 354; Sitz. Ber. 9, 286).

Canaigre tannin is present in the tuberous roots of the *Rumex hymenosepalus* (Torr.), an important American tanning material. It has been submitted to an elaborate examination by Trimble (The Tannins, 1894, ii. 115), who describes it as a yellowish-white powder readily soluble in water, which gives with lead acetate solution a yellow precipitate, and with ferric chloride a green precipitate. It reacts with bromine water to give a yellow deposit, and on heating to 160°–190° is decomposed with production of *catechol.* Boiling 2 p.c. hydrochloric acid yields an insoluble red phlobaphane together with some *protocatechuic acid.* Sugar is not formed in this decomposition. Analysis gave C=58·10 ; H=5·33, figures which approximate to, though they are somewhat lower than, those given by the best known phlobatannins.

Catechu-tannic acid (see CATECHU).

Cherry-bark tannin $C_{21}H_{20}O_{10}+\frac{1}{2}H_2O$ is present in the bark of the *Prunus Cerasus* (Linn.) (Rochleder, Sitz. Ber. 59, 819) and gives a green coloration with ferric chloride. It is not a glucoside but when digested with boiling dilute acids gives a red phlobaphane $C_{21}H_{18}O_8+\frac{3}{4}H_2O$.

Cocatannic acid $C_{17}H_{22}O_{10}+2H_2O$ (?) present in the leaves of the *Erythroxylon Coca* (Linn.) (Niemann, Jahrb. Min. 1860, 386), is sparingly soluble in cold water and gives a green coloration with ferric salts. According to Warden (Pharm. J. 18, 985) it can be obtained in microscopic crystals of a sulphur yellow colour.

Colatannin or **Kolatannin** $C_{16}H_{20}O_8$, a light red amorphous powder, exists in the Kola nut, *Cola acuminata* (Schott and Endl.), in combination probably with caffeine and theobromine (Knox and Prescott, J. Amer. Chem. Soc. 1897, 19, 63). With ferric acetate it gives a green coloration, and on fusion with alkali *protocatechuic acid* is obtained. *Penta-acetylkolatannin* $C_{16}H_{15}O_8(C_2H_3O)_5$ colourless powder, *tribromkolatannin* $C_{16}H_{17}O_8Br_3$ red-brown powder, *penta-acetyl-tribromkolatannin* $C_{16}H_{12}O_8Br_3(C_2H_3O)_5$, *pentabrom*, and *hexabromkolatannin* have been described. On heating, kolatannin yields various anhydrides $(C_{16}H_{19}O_7)_2O$ at 107°–110°, $(C_{16}H_{17}O_6)_2O$ at 135°–140° and $C_{16}H_{16}O_6$ at 155°–156°.

Cortepinitannic acid $C_{32}H_{34}O_{17}$ occurs together with pinicortannic acid in the bark of the Scotch fir, *Pinus sylvestris* (Linn.). It consists of a bright red powder, the aqueous solution of which gives an intense green coloration with ferric chloride (Kawalier, Sitz. Ber. 11, 363).

Euphrasia tannin is present according to Enz (Vierteljarsch. Pharm. J. 8, 175) in the green parts of *Euphrasia officinalis* (Linn.), and gives a green colour reaction with ferric salts. Its lead salt has the composition $C_{32}H_{20}Pb_3O_{20}$.

Fragarianin *v. Strawberry tannin.*

Filitannic acid $C_{41}H_{36}NO_{18}$ (?) exists in fern-root (*Aspidium filix mas* (Swartz.)) (Malin, Annalen, 143, 276), and forms a red-brown powder which, in aqueous solution, gives an olive green coloration with ferric chloride. By boiling with dilute sulphuric acid it gives *filix red* $C_{20}H_{18}O_{12}$, an amorphous compound, and this when fused with alkali gives *phloroglucinol* and *protocatechuic acid* (*cp.* also Reich, Arch. Pharm. 1900, 238, 648).

Fraxitannic acid $C_{26}H_{32}O_{14}$ (?) occurs in the leaves of the ash tree *Fraxinus excelsior* (Linn.). It consists of a brownish-yellow deliquescent powder, and when heated at 100° loses water and forms an almost insoluble anhydride $C_{26}H_{30}O_{15}$ (Gintl and Reinitzer, Monatsh. 3, 745). Aqueous ferric chloride produces a dark green coloration, and when oxidised with permanganate this tannin yields quinone. *Acetylfraxitannic acid* $C_{26}H_{28}O_{14}(C_2H_3O)_4$, *benzoylfraxitannic acid* $C_{26}H_{28}O_{14}(C_7H_5O)_4$, *tribromfraxitannic acid* $C_{26}H_{29}Br_3O_{14}$, and *tetra-acetyltribromfraxitannic acid*

$$C_{26}H_{25}Br_3O_{14}(C_2H_3O)_4$$

have been described.

Galitannic acid $C_{14}H_{16}O_{10},H_2O$ exists in the bark of the *Galium verum* (Linn.) (Schwarz, Annalen, 83, 57). It gives a yellow precipitate with basic lead acetate and a green colour reaction with ferric chloride.

Guarana tannin is present in the *Paullinia Cupana* (H. B. and K.), the seeds of which, known as 'guarana,' contain theine and are extensively used in South America for medicinal purposes. According to Nierenstein (Die Gerbstoffe, 20) the tannin consists of small colourless crystals, m.p. 199°–201°, and yields an acetyl derivative, m.p. 134°–136°. It is lævorotatory, having $[\alpha]_D^{20} = -72{\cdot}4°$ in water, and $[\alpha]_D^{20} = -39{\cdot}1°$ in alcohol.

Hemlock tannin $C_{20}H_{18}O_{10}$ (?) is present in Hemlock bark, *Tsuga* [*Abies*] *canadensis* (Carr), the extract of which is prepared on a very large scale in North America for tanning purposes. According to Böttinger (Ber. 1884, 17, 1125), it is probably related to the quercitannic acid of the oak and on heating with sulphuric or hydrochloric acid gives the anhydride *hemlock red* $C_{40}H_{30}O_{17}$. With hydrochloric acid at 180°, hemlock red evolves methyl chloride : when heated with acetic anhydride the acetyl compound $C_{40}H_{23}O_{17},(C_2H_3O)_7$ is produced, whereas bromine gives a mixture of the compounds $C_{40}H_{20}Br_{10}O_{17}$ and $C_{40}H_{16}Br_{14}O_{17}$. Bromine added to the diluted tannin extract precipitates *tetrabromhemlock tannin* $C_{20}H_{14}Br_4O_{10}$, a yellow powder which yields the *penta-acetyl* derivative $C_{20}H_9Br_4O_{10}(C_2H_3O)_5$, and by the further action of bromine the bromine compound $C_{20}H_{12}Br_6O_{10}$ (*cp.* Trimble, Amer. J. Pharm. 1897, 69, 354, 406 ; J. Soc. Chem. Ind. 1898, 17, 558) is produced.

Hop-tannin $C_{22}H_{26}O_9$ present in hops (*Humulus Lupulus* [Linn.]) (Etti, Annalen, 180, 223 ; Monatsh. 10, 651) has all the properties of a catechol tannin. It gives with ferric chloride a dark green coloration and with boiling dilute mineral acid the phlobaphane 'hop red' $C_{32}H_{26}O_{15}$. Hop red forms a cinnamon coloured powder and on fusion with potash yields *phloroglucinol* and *protocatechuic acid.*

Horse chestnut tannin $C_{26}H_{24}O_{12}$ is present in nearly all parts of the *Aesculus Hippocastanum* (Linn.) and in the root bark of the apple tree (Rochleder, Sitz. Ber. 53, [ii.] 478 ; 54, [ii.] 609). It consists of a nearly colourless powder, the solution of which gives a green coloration with ferric chloride, and when boiled with dilute mineral acid the phlobaphane $C_{26}H_{22}O_{11}$ or $C_{26}H_{20}O_{10}$. On fusion with alkali, *phloroglucinol* and *protocatechuic acid* are produced. *V.* also *phyllæscitannin* and article CHESTNUT EXTRACT.

Ipecacuanhic acid $C_{14}H_{18}O_7$ was obtained by Willigt (Annalen, 76, 345) from the roots of *Psychotria Ipecacuanha* (Stokes), and consists of a reddish-brown, bitter hygroscopic substance. Its solution gives a green coloration with ferric chloride.

Japonic acid (see CATECHU).

Kino v. Article.

Larch tannin. The bark of the larch *Larix europaea* (DC.) contains considerable quantities of a tannin which was examined by Stenhouse (Phil. Mag. 23, 336). It forms an olive green precipitate with ferric salts, and when boiled with dilute sulphuric acid a red phlobaphane is produced.

Maletto tannin occurs in the bark of *Eucalyptus occidentalis* (Endl.) and other species of eucalyptus. According to Strauss and Geschwender (Zeitsch. angew. Chem. 1906, 19, 1121) it possesses the formula $(C_{43}H_{50}O_{20})_2$ and appears to be identical with quebracho tannin. Dekker (Arch. Néerland, 1909, ii. 14, 50) prefers the formula $(C_{19}H_{20}O_9)_n$ and describes the acetyl derivative $C_{38}H_{23}O_{17}Ac_{10}$ and benzoyl derivative

$$C_{19}H_{25}O_{12}Bz_5.$$

Heated with zinc dust and sodium hydroxide solution the tannin gives small quantities of *gallic acid* and *phloroglucinol*, whereas dry distillation yields *pyrogallol* and traces of other phenols. Boiling dilute sulphuric acid forms 'malleto red' $C_{57}H_{50}O_{22}$ from which the *acetyl* derivative $C_{57}H_{35}O_{22}Ac_{15}$ can be obtained.

Mangrove tannin $C_{24}H_{26}O_{12}$. This important tannin is derived from the *Rhizophora Mangle* (Linn.), *R. mucronata* (Lam.), *Ceriops Candolleana* (Arn.), *C. Roxburghiana* (Arn.), and other allied species. It is described as an amorphous red powder, which on fusion with alkali gives *protocatechuic acid*, and with boiling dilute sulphuric acid the phlobaphane $C_{48}H_{46}O_{21}$. The *monacetyl* derivative $C_{24}H_{25}O_{12}(C_2H_3O)$ melts at 205° (Nierenstein. Die Gerbstoffe). This tannin closely resembles in its properties catechutannic acid (*see* CATECHU) and indeed mangrove cutch and catechu may be employed in many cases for the same purpose. Possibly these two substances are identical and Procter (private communication) has isolated from mangrove cutch a small quantity of a colourless crystalline substance resembling catechin. Perkin who examined an ethyl acetate extract of the fresh bark of the *C. Candolleana*, prepared in Borneo, was unable to detect the presence of a catechin, but obtained the tannin as a pale yellow powder, which gave a green coloration with ferric chloride solution, and resembled catechutannic acid in many respects.

Mimosa tannin is derived from various species of *Mimoseae*, such as the *Acacia arabica* (Willd.) of Egypt, the so-called 'Wattles' of Australia, and numerous others. The tannin present is interesting in that though it possesses the reactions of a phlobatannin, such as phlobophane production, precipitation by bromine water and solubility of its lead compound in acetic acid, &c., it gives a bluish-violet coloration with ferric chloride. Ammonium sulphide gives a precipitate with a mimosa solution when after removal of the excess by boiling, a few drops of sulphuric acid are added, followed by a small quantity of salt. All other phlobatannins, except Maletto and Pistaschia tannins, give no precipitate by this method (Stiansy, private communication).

Moritannic acid, see *Maclurin*, art. OLD FUSTIC (Old Fustic is apparently not a tannin matter).

Oxypinitannic acid v. *Pinitannic acid.*

Oak bark tannin or *Quercitannic acid* is found in the bark of the oak, and is not to be confused with the tannin of oak-wood from which it is distinct, and which is described below under the name of quercinic acid. In 1792, George Swayne communicated to the Society of Arts his results on the use of oak leaves in tanning (Trimble, The Tannins, ii. 51), and it was again discussed by Berzelius in his Lehrbuch, 1827, and by Liebig (Handbuch der Chemie, 1843). Assumed at that time to be identical with the tannin of nut-galls (gallotannin), it was first shown by Stenhouse (Phil. Mag. 22, 425) to differ from this substance. According to Grabowski (Sitz. Ber. 56, [ii.] 388), Oser (*ibid.* 72, [ii.] 178), Johanson (Arch. Pharm. [iii.] 9, 210), Böttinger (Ber. 14, 1598), quercitannic acid is in reality a glucoside, but Etti (Ber. 14, 1826; Monatsh. 4, 512) showed that the pure substance did not yield a trace of sugar. Various formulæ have been assigned to this substance, viz. Eckert (J. 1864, 608) $C_{28}H_{20}O_{20}$; Oser (J. 1875; 600) $C_{30}H_{20}O_{11}$; Löwe (Zeitsch. anal. Chem. 20, 210) $C_{25}H_{30}O_{15}$; Böttinger (Ber. 1883, 16, 2712) $C_{15}H_{12}O_9,2H_2O$, and Etti (Monatsh. 10, 650) $C_{17}H_{16}O_9$, $C_{18}H_{18}O_9$ and $C_{20}H_{20}O_9$.

Quercitannic acid is described by Etti as a reddish-white powder almost insoluble in water. One of its most characteristic properties is the readiness with which it forms reddish-brown anhydrides when heated by itself or with dilute acids. Thus at 130°–140° the *first anhydride* $C_{34}H_{30}O_{17}$ is produced, and this by heating with dilute sulphuric or hydrochloric acid gives the *second anhydride* $C_{34}H_{28}O_{16}$. Boiling dilute sulphuric acid again converts the original tannin into the *third anhydride*

$$2C_{17}H_{16}O_9-3H_2O=C_{34}H_{26}O_{15}.$$

These compounds are insoluble in water, but coloured a solution of ferric chloride blue. Löwe (*l.c.*) again examined an anhydride $C_{28}H_{24}O_{12}$ and an 'oak red' $C_{28}H_{22}O_{11}$. Böttinger, who prepared the oak red from the tannin by means of dilute sulphuric acid, adopted the formula $(C_{14}H_{10}O_6)_2,H_2O$. Etti (Ber. 1884, 17, 1823) isolated from the bark of the *Quercus pubescens* (Willd.) a tannin $C_{20}H_{20}O_9$, practically identical with the substance $C_{17}H_{16}O_9$ previously found in the *Q. robur* (Linn.), but giving a green solution with ferric chloride, and not a blue, as formerly stated.

When heated with dilute sulphuric acid at 130°–140°, quercitannic acid gives in addition to anhydride 1·5 p.c. of *gallic acid*, and with strong hydrochloric acid at 150°–180° the formation of oak red was accompanied by the evolution of methyl chloride (Etti, Monatsh. 1, 274). On dry distillation it yields *dimethylcatechol* and *catechol*, and on fusion with alkali *protocatechuic acid*, *catechol*, and *phloroglucinol*.

By the action of bromine on the aqueous bark extract, Böttinger (Ber. 1883, 16, 2710) obtained *dibromquercitannic acid* $C_{19}H_{14}Br_2O_{10}$ as a yellow precipitate, and from this *pentaacetyldibromquercitannic acid* was prepared. Heated with hydrochloric acid at 180°, *methyl chloride* was evolved, and by means of hydroxylamine hydrochloride the compound

$$C_{19}H_{15}Br_2NO_{10}$$

was produced. Reduced with sodium amalgam *hydroquercinic acid* $C_{15}H_{14}O_7$ or $C_{15}H_{16}O_6$ ar *hydroquergalic acid* $C_{14}H_{14}O_6$ are formed (Annalen, 263, 121). When suspended in chloroform and further brominated it yields tetrabromdehydroquercitannic acid. Quercitannic acid was thus $C_{19}H_{16}O_{10}$, contained five hydroxyls, and the group $COOCH_3$.

According to Etti (Monatsh. 10, 647), a further investigation of the tannins $C_{17}H_{16}O_9$ and $C_{20}H_{20}O_9$ has proved that they are not glucosides, but derivatives of a ketonic acid

$$C_6H_2(OH)_3CO{\cdot}C_6H(OH)_3COOH.$$

Trimble (The Tannins, 1894, ii. 77) carried out an elaborate investigation of the tannins present in the barks of the *Quercus alba* (Linn), *Q. coccinea* (Wargenh.), *Q. discolor* (Ait.), *Q. falcata* (Michx.), *Q. palustris* (Du Roi), *Q. Prinus* (Linn.), *Q. bicolor* (Willd.), *Q. obtusiloba* (Michx.), *Q. phellos* (Linn.), *Q. rubra* (Linn.), *Q. robur* (Linn.), *Q. semicarpifolia* (Sm.), employing acetone for the purpose of extraction. The tannins in most cases had a pale yellow colour, gave with ferric chloride a *green* coloration, and practically identical results with all the usual tannin reagents.

Heated with glycerol at 160°, the tannins of *Q. tinctoria*, *Q. palustris*, *Q. falcata* and *Q. phellos* yielded *catechol*, whereas with fused alkali the eight samples examined gave *protocatechuic acid*. Though all these compounds produce a violet colour on pine wood moistened with hydrochloric acid, phloroglucinol or other phenol was not detected among their decomposition products. Heated with 2 p.c. hydrochloric acid for two and a half hours, a phlobaphane separated, whereas the solution contained protocatechuic acid. Analyses of nine of these tannin preparations showed but little variation, the average being C=59·79; H=5·08, and approximately correspond with those of Etti (*l.c.*) for the tannin $C_{20}H_{20}O_9$ from *Q. pubescens*, and of Kraemer (Amer. J. Pharm. 1890, 236) for the tannin of *Q. alba*.

Oak wood tannin, *Quercin*, *Quercic acid*, *Quercinic acid* $C_{15}H_{12}O_9,2H_2O$ consists of a light brownish-yellow substance, and is distinguished from the quercitannic acid of oak bark in that its aqueous solution gives a blue, not green, coloration with ferric chloride, and does not yield a precipitate with bromine water (Böttinger, Ber. 1887, 20, 761).

With the object of isolating the tannin in a pure condition Böttinger acetylated a purified extract of the wood, and decomposed the acetyl compound $C_{15}H_7(C_2H_3O)_5O_9$ by heating it with water at 135°. By the action of sodium amalgam on the acetyl derivative, Böttinger (Annalen, 263, 110) obtained *hydroquercic acid* $C_{15}H_{18}O_7$ or $C_{15}H_{16}O_6$, *querlactone* $C_5H_6O_2$ and an acid which is probably trihydroxybutyric acid.

Hydroquercic acid is a grey-brown, bitter, hygroscopic powder, which forms the *acetyl* derivative $C_{15}H_{14}(C_2H_3O)_2O_6$, the *barium* salt $(C_{15}H_{15}O_6)_2Ba$, and the *lead* salt $(C_{15}H_{15}O_6)_2Pb$. Querlactone, on the other hand, forms the salt $(C_5H_7O_3)_2Pb$. As above noted, hydroquercinic acid could also be obtained in a similar manner from quercitannic acid.

Etti (Monatsh. 10, 647) isolated from the wood of the Slavonian oak a tannin $C_{16}H_{14}O_9$ which appeared to be a ketonic compound. This is present in wood in the form of a readily soluble salt (probably magnesium salt). Crystallised from alcohol, it forms brownish-red microscopic warty spherical masses, insoluble in water, and having the properties of a monobasic acid (*cf.* Fuchs, Monatsh. 9, 1132). With phenylhydrazine it gives the compound

$$C_{22}H_{20}N_2O_8,$$

forms a brown amorphous oxime $C_{16}H_{15}NO_9$ and with dilute sulphuric acid at 120°–130° yields *gallic acid* in addition to a red anhydride. Heated alone at 130°–135°, or in a sealed tube with water at 100°, anhydrides are also produced, which on boiling with hydriodic acid evolve methyl iodide. On long digestion of the tannin $C_{16}H_{14}O_9$ with hydrochloric acid at 100°, a methoxyl group is split off, with production of an acid $C_{15}H_{12}O_9$ of a yellow colour in which a methoxyl group is still present. This tannin is therefore probably the dimethyl ether of the ketonic acid formulated above.

On boiling the tannin with dilute sulphuric acid, the anhydride $C_{32}H_{24}O_{16}$ is produced, whilst on heating in a closed tube the anhydrides $C_{32}H_{20}O_{14}$ and $C_{32}H_{18}O_{13}$ were obtained.

The varied results of many of these workers with the oak tannins appear to be due, as suggested by Trimble, to the fact that in many cases they employed oak tannin extracts of doubtful authenticity. Thus it is possible that Etti, who in his earlier work describes the tannin as producing a blue coloration with ferric chloride, was in reality examining oak wood and not oak bark preparations, and again the peculiar insoluble property of certain of his tannins, also commented on by Trimble, suggests that in these cases he investigated an anhydride rather than the tannin itself. That oak barks contain only a phlobatannin appears to be certain from the investigations of Trimble, and it seems probable that in the wood a pyrogallol tannin alone exists. Though, as stated above by Etti in the case of the Slavonian oak, this yields phlobaphanes, Stiasny (private communication) has found that such is not usually the property of oak-wood extracts. An interesting point, moreover, apparently not stated in the literature, though well known to tanners, is that oak-wood extracts give some ellagic acid, and on this account impart to leather the 'bloom' so characteristic of this substance.

Oenotannin $C_{19}H_{16}O_{10}$ (?) was obtained by Gautier from red wine (Bull. Soc. chim. 1877, 27, 496), who describes it as a colourless substance readily soluble in water. It gives a green coloration with ferric chloride solution, by fusion with alkali *protocatechuic acid* and *phloroglucin*, and when exposed to moist air becomes converted into an insoluble red phlobaphane-like substance. According to Heise (Ber. Ref. 22, 823), oenotannin contains gallotannin and is a mixture of three substances.

Pistachia tannin is present in the leaves of the *Pistacia Lentiscus* (Linn.) in addition to some quantity of a gallotannin (Perkin and Wood, Chem. Soc. Trans. 1898, 73, 378), and consists of a pale-brown brittle mass which with iron alum solution give a blue-black coloration. With boiling dilute sulphuric acid a phlobaphane quickly separates, and when fused with alkali *gallic acid* and *phloroglucinol* are produced.

Phyllæscitannin is the name given by Rochleder to a tannin present in the small leaflets of the horse chestnut, as long as they remain enclosed in the buds (Zeitsch. Chem. 1867, 84). It is described as an amorphous red-brown substance of the formula $C_{26}H_{24}O_{13},H_2O$, having a strongly astringent taste.

Pinicortannic acid and **cortepinitannic acid** occur in the bark of the Scotch fir *Pinus sylvestris* (Linn.), and can be separated owing to the fact that in aqueous solution the former only is precipitated by means of lead acetate. Pinicortannic acid forms a reddish-brown powder of the composition $(C_{16}H_{18}O_{11})_2,H_2O$, which after drying is sparingly soluble in water. It gives a green coloration with ferric chloride, and when boiled with dilute acids gives the phlobaphane $C_{48}H_{50}O_{21}$ (Kawalier, Sitz. Ber. 11, 361).

Pinitannic acid and **oxypinitannic acid** occur in the needles of the Scotch fir *Pinus sylvestris* (Kawalier), and are distinguished from one another by the fact that the former only is precipitated by lead acetate solution. *Pinitannic acid*, according to Rochleder (Sitz. Ber. 29, 60), also present in the *Thuja occidentalis*, is a reddish-yellow substance which gives a red-brown coloration with ferric chloride and when boiled with dilute acids a sparingly soluble red product (phlobaphane).

Oxypinitannic acid, on the other hand, forms a green solution with ferric chloride (Kawalier).

Quebracho tannin or *Quebrachitannic acid*, see QUEBRACHO COLORADO.

Quinotannic acid or *Cinchonatannic acid* obtained from cinchona bark is a light yellow very hygroscopic substance, a solution of which gives a green precipitate with ferric salts. On digestion with boiling dilute sulphuric acid, it is converted into a sugar and cinchona red $C_{28}H_{22}O_{11}$ (Rembold, Annalen, 143, 270), and from the latter by fusion with alkali, *protocatechuic* and acetic acids are produced (Hlasiwetz, *ibid.* 143, 307). According to Schwarz (Sitz. Ber. 7, 250), quinotannic acid has the composition $C_{14}H_{16}O_9$, whereas cinchona red is to be represented as $C_{12}H_{14}O_6$.

Quinovatannic acid, contained in the bark of the *Cinchona nova*, in many respects resembles quinotannic acid (Hlasiwetz, Annalen, 79, 129). With ferric chloride it gives a dark green coloration and with boiling dilute acids quinova red $C_{12}H_{12}O_5$ is produced. On fusion with potash it yields *protocatechuic acid*.

Rhamnotannic acid (so called) present in buckthorn berries is, in reality, not a tannin matter.

Rhatany tannin $C_{20}H_{20}O_9$ from the bark of rhatany root, *Krameria triandra* (Ruis and Pav.) (Willstein, J. 1854, 656) is described by Raabe (*ibid.* 1880, 1060) as a light yellow powder, readily soluble in water. Its solution gives with ferric chloride a green coloration. When heated with dilute acids it yields rhatany red $C_{22}H_{22}O_{11}$ and a sugar (Grabowski, Annalen, 143, 274), whereas according to Raabe (*l.c.*) no sugar is thus produced and the red substance possesses the composition $C_{26}H_{18}O_8$. By dry distillation rhatany red yields catechol, *protocatechuic acid* and *phloroglucinol* when fused with alkali.

Rheotannic acid or *Rhubarb tannic acid* $C_{26}H_{26}O_{14}$, derived from rhubarb, forms a yellowish-brown readily soluble powder, the solution of which gives with ferric chloride a black green precipitate. With boiling dilute acids it gives *rheic acid* (rheumic acid) $C_{20}H_{16}O_9$ and a fermentable sugar (Kubly, Zeitsch. Chem. 1868. 308), although according to Tschirch and Neuberger (Schweiz. Wochenschr. Chem. Pharm. 1902, 282) in this manner *rheum-red* $C_{40}H_{32}O_{18}$, *cinnamic acid*, *gallic acid* and sugar are produced. According to Gilson (Chem. Zentr. 1903, i. 722, 882), two glucosides are present, *glucogallin* $C_{13}H_{16}O_{10}$, giving gallic acid and dextrose, and *tetrarin* $C_{32}H_{32}O_{12}$ from which *rheosurin* $C_{10}H_{12}O_2$, *cinnamic acid*, and *gallic acid* can be produced. According to Krembs (Inaugural Diss. 1903, Berne), a catechin is also present in rhubarb.

Rhodotannic acid $4C_{14}H_{12}O_7,3H_2O$, found in the leaves of *Rhododendron ferrugineum* (Linn.) is an amber coloured substance which gives a green coloration with ferric chloride solution. Heated with dilute mineral acids, a reddish-yellow precipitate of *Rhodoxanthin* $C_{14}H_{14}O_8$ is produced (Schwarz, Sitz. Ber. 9, 298).

Rubinic acid *v.* CATECHU.

Rubitannic acid $2C_{14}H_{22}O_{12}+H_2O$ was obtained by Willigt (Annalen, 82, 340) from the leaves of *Rubia tinctorum* (Linn.). It gives a green colour reaction with ferric chloride.

Sequiatannic acid $C_{21}H_{20}O_{10}$ was isolated from the cones of *Sequoia gigantea* (Torr) (California) by Heyl (Pharm. Centr. 1901, 42, 379) as a reddish-brown powder, soluble in water and yielding the salts $MgC_{21}H_{18}O_{10}$ and $CaC_{21}H_{18}O_{10}$. Boiled with dilute sulphuric acid, a *phlobaphane, gallic acid*, and a sugar are produced. The *hexa-acetyl* $C_{21}H_{14}O_{10}(C_2H_3O)_6$, *hexabenzoyl* $C_{21}H_{14}O_{10}(C_7H_5O)_6$ and *bromine* $C_{21}H_{15}O_{10}Br_5$ derivatives of this tannin are amorphous.

Sorbitannic acid from the juice of the ripe berries of the mountain ash *Sorbus Aucuparia* (Linn.) forms a thick syrupy mass, which gives a green coloration with ferric chloride solution. It yields *catechol* on dry distillation, and *protocatechuic acid* and *phloroglucinol* when fused with alkali (Vincent and Delachanal, Bull. Soc. chim. [ii.] 47, 492).

Spruce-bark tannin $C_{21}H_{20}O_{10}$ (?) gives, according to Böttinger, an unstable bromo derivative $C_{21}H_{14}Br_6O_{10}$. This reacts with hydroxylamine hydrochloride, and with hydrochloric acid at 180°–190° evolves *methyl chloride.* The penta-acetylpentabromo derivative

$$C_{21}H_{10}Br_5O_{10}(C_2H_3O)_5$$

was also prepared. With boiling dilute hydrochloric acid the tannin yields *spruce red* which yields the acetyl derivative $C_{42}H_{27}(C_2H_3O)_7O_{17}$, and when suspended in chloroform and treated with bromine the compound $C_{42}H_{24}Br_{10}O_{17}$ (Böttinger, Ber. 17, 1127).

Strawberry-root contains a tannin *fragarianin* (Phipson, J. 1878, 891), the solution of which gives a green colour with ferric chloride. Boiling dilute hydrochloric acid forms *glucose* and a red substance *fragiarin.* On dry distillation the tannin gives traces of *catechol*, and when fused with alkali *protocatechuic acid* is produced.

Tannecortepinic acid $C_{28}H_{26}O_{12}$, according to Rochleder and Kawalier (Sitz. Ber. 29, 23), can be isolated from the bark of young Scotch firs collected in the spring time. Ferric chloride gives a green coloration and boiling dilute acid a phlobaphane in addition to a little sugar.

Tannopinic acid $C_{26}H_{30}O_{12}$(?) is sometimes present in the needles of the Scotch fir gathered in the spring (Rochleder and Kawalier). In the winter time, oxypinitannic acid appears to take its place.

Tea-tannin is probably identical with the quercitannic acid of oak bark (Stenhouse, Phil. Mag. 23, 332; Rochleder, Annalen, 63, 205; and Hlasiwetz and Malin, J. pr. Chem. [i.] 101, 109).

Tormentilla tannin $C_{26}H_{22}O_{11}$, from the root of *Potentilla Tormentilla* (Neck.), is an amorphous reddish powder, which colours ferric chloride solution blue green. Boiled with dilute acids it produces *tormentil-red* without appreciable formation of sugar, and this appears to have the same composition as the tannin itself. With fused alkali *phloroglucinol* and *protocatechuic acid* are obtained. The root also contains a substance which yields *ellagic acid* when boiled with potash solution (Rembold, Annalen, 145, 5).

Viridic acid $C_{14}H_{20}O_{11}$ (?), which exists in coffee beans as a calcium salt (Rochleder, Annalen, 63, 197) and is obtained by the air oxidation of an ammoniacal solution of caffetannic acid, forms a brown amorphous mass, the alkaline solutions of which are green. The salts $Ba_2C_{14}H_{16}O_{11}$, $PbC_{14}H_{12}O_8$, and $PbC_{14}H_{14}O_9$ have been described (*cf.* also Vlaanderen and Mulder, J. 1858, 261).

Willow bark tannin. The bark of *Salix triandra* (Linn.) contains a glucoside tannin which gives a green colour reaction with ferric chloride, and when boiled with dilute sulphuric acid a brown-red precipitate (Stenhouse, Proc. Roy. Soc. 11, 403; Johanson, Arch. Pharm. [iii.] 13, 103).

Tannins are frequently accompanied in the plant by yellow colouring matters, and it has been pointed out by Perkin that a relationship is usually to be observed between these compounds in respect of the phenolic nuclei present in each. Thus catechu contains catechutannic acid and quercetin, both of which contain phloroglucinol and catechol groups, whereas both the cyanomaclurin and morin of Jâk wood (*Artocarpus integrifolia* (Linn.)) yield phloroglucinol and β-resorcylic acid. Again in sumach (*R. Coriaria* (Linn.)) *Pistacia lentiscus* (Linn.) (leaves) and *Hæmatoxylon campeachianum* (Linn.) (leaves), a gallotannin and myricetin exist, both of which are pyrogallol derivatives.

Other similar instances of this relationship could be cited; and where a divergence of this rule at first sight seems evident, this is frequently more apparent than real, as in the case of Young Fustic (*R. cotinus* (Linn.)) which is known to contain a gallotannin and fisetin (catechol and phloroglucinol). From the reactions of the wood extract, however, catechol tannin must also be present. A. G. P.

TANNISMUT, TANNOFORM, TANNOPIN, TANNOSAL, TANNOGUAIAFORM, TANNOCRESOFORM, TANNIGEN, TANNALBIN, TANARGAN, TANNOCASUM, TANNOTHYMAL, TANNYL, TANOCOL *v.* SYNTHETIC DRUGS.

TANTALITE. A heavy, black mineral consisting essentially of iron tantalate $FeTa_2O_6$, and crystallising in the orthorhombic system. The ferrous iron is usually in part, or sometimes almost wholly, replaced by manganous oxide, forming a passage to the variety known as *manganotantalite*. In the same way, tantalic acid is replaced isomorphously by columbic acid, forming a gradual passage into the species columbite (*q.v.*). The general formula for this isomorphous group is thus $(Fe,Mn)(Ta,Cb)_2O_6$. With the variation in the relative amounts of columbic and tantalic acids the sp.gr. ranges from 5·3 (columbite) to about 7·8 for nearly pure tantalite. In their other physical and crystallographic characters the two species are, however, remarkably similar. They are iron-black to brownish-black with a sub-metallic lustre, and a dark brown to black streak; H.=6. They are usually found as crystalline grains, or forming large rough masses by the sub-parallel grouping of prismatic crystals; well-formed crystals with brilliant faces are occasionally met with. They occur embedded in granitic rocks, more especially in pegmatite-veins intersecting these rocks: a common associated mineral is cassiterite. The columbium-rich members are of much more frequent occurrence than those at the tantalum end of the series.

Tantalite has long (since 1802) been known from several localities in Finland, and it has also been found in a few other countries. The greatly increased demand for tantalum since its introduction in the metallic filament electric lamps in 1904 has led to the discovery of several new localities, more particularly in Australia; and it is this continent that now supplies most of the raw material. It has been obtained in commercial quantities at Wodgina in the Pilbara gold-field, and at Greenbushes in the Blackwood Ranges, in Western Australia; and on the Finniss river near Port Darwin in Northern Territory. At Wodgina it occurs in pegmatite-veins, composed of quartz, felspar (mainly albite), mica (muscovite and lepidolite) and tantalite, the last-named in crystalline masses from the size of a shot to those weighing 5 cwts. The tantalite is collected from the surface soil, from the neighbouring alluvial deposits, and by quarrying the pegmatite. At Greenbushes it is found as grains and irregular lumps, reaching 13 lbs. in weight, in the alluvial deposits of tin-stone. On the Finniss river the mineral occurs with cassiterite scattered through a large intrusion of greisen.

Analyses: I. Tantalite ('skogbölite') from Skogböle, Kimito, Finland (A. Nordenskiöld, 1857). II. Grizzly Bear Gulch, Black Hills, South Dakota (W. P. Headden, Amer. J. Sci. 1891, 41, 98). III. Greenbushes, Western Australia (E. S. Simpson, Rep. Austr. Assoc. Adv. Sci., 1908, 11 (for 1907), 442; and Chem. News, 1909, 91, 49). IV. Manganotantalite from Wodgina, Western Australia (E. S. Simpson, *l.c.*). V. Manganotantalite from Finniss river, North Australia (Rep. Govt. Geologist, South Australia, 1905).

	I.[1]	II.	III.[2]	IV.	V.
Ta_2O_5	84·44	82·23	80·61	69·95	55·52
Cb_2O_5	—	3·57	2·50	14·47	24·92
SnO_2 .	1·26	0·32	1·51	0·36	4·40
FeO .	13·41	12·67	10·89	2·68	2·72
MnO .	0·96	1·33	3·78	(12·54)	11·16
Total	100·36	100·12	100·48	100·00	98·72
Sp.gr.	7·85	8·20	7·74	7·09	—

[1] Also CuO, 0·14; CaO, 0·15.

[2] Also TiO_2, 0·71; WO_3, 0·13; H_2O, 0·14; NiO, 0·02; MgO, 0·19.

References. Occurrence and Uses of Tantalum, Bull. Imp. Inst. London, 1907, 5, 429. For Australian occurrences, *see* E. S. Simpson, *l.c.* and 1910, 12 (for 1909), 310. L. J. S.

TANTALUM. Sym. Ta. At.wt. 181·5 (Balke). Shortly after the discovery of columbium by Hatchett, in 1801–2, a metal of similar properties was discovered by Ekeberg in certain Swedish minerals resembling those from which columbium had been isolated, and was called by him tantalum, on account of its extreme resistance to acids. Notwithstanding the fact that tantalite, the mineral which gave the largest yield of the new metal, was much heavier than columbite, Wollaston in 1809 concluded that the two metals were identical, and for many years they were indifferently termed columbium or tantalum. The similarity between the compounds of these metals, their invariable occurrence together in minerals, and the difficulty experienced in separating them from each other and the associated metals, prevented the large amount of work which was done upon them from yielding conclusive results, and it was not until the middle of the century that their true relations were established.

Although belonging to the group which includes vanadium, phosphorus, arsenic, antimony, bismuth, and nitrogen, tantalum and columbium have few properties in common with those elements, and invariably occur with minerals belonging to entirely different groups. Commercially speaking, they are members of a group of heavy metals, which includes tungsten, molybdenum, and uranium, found only in the oldest plutonic rocks. These metals are characterised by the power of improving and hardening steel when added in extremely small quantities, and it is interesting to note that the minerals carrying them commonly contain the metals of the rare earths, and rare alkaline earths, or are associated with minerals containing them. Zirconia, thoria, ceria, and even lithia, together with practically all the other rare earths and alkaline earths, occur in the same parent rocks, and it is probable that this common, indeed almost invariable association, is intimately connected with the origin of these metals.

The use of tantalum and columbium for hardening steel, their high melting-points, and the possibility of working the pure metals, either alone or in alloy with each other, into wire, and vessels of great acid-resisting properties, have recently given an impetus to the search for minerals containing them, which has resulted, for the moment, in the working of more deposits than the market can utilise. There is little doubt, however, that the larger output will ultimately result in an increased demand, as the uses to which the metals can be applied are so numerous. The value of apparatus made from these metals for chemical, physical, and surgical purposes in undoubted, and is likely to result in a demand for even larger quantities of the mineral than are at present available.

As regards the occurrence of tantalum in nature, the article on COLUMBIUM may be consulted. The two metals occur together and, although one may predominate in a mineral to an extent which renders it the characteristic metal, it is extremely exceptional to find one without a considerable proportion of the other.

For many purposes, it is probable that an alloy of tantalum and columbium is suitable, but it is usual to separate the oxides or salts before reduction to metal, and, as tantalum is preferred for most purposes, it is fortunate that its proportion in the minerals now worked largely predominates. Like columbium, tantalum occurs in nature only as the pentoxide, and all the minerals in which it is found may be regarded as tantalates or, in a few rare minerals, as silico-tantalates.

Although tantalum occurs as an essential, or at any rate invariable, constituent in a large number of the heavy rare minerals, the only one which is worked commercially is tantalite, essentially a tantalate of iron and manganese $Ta_2O_5(FeMn)O$, which may contain as much as 84 p.c. of Ta_2O_5, although seldom exceeding 70 p.c. The proportion between the iron and manganese varies considerably, and the tantalum may be largely replaced by columbium. In other words, tantalite may merge into *skogbolite* $Ta_2O_5\cdot FeO$, containing up to about 85 p.c. of Ta_2O_5, *manganotantalite* $Ta_2O_5\cdot MnO$ (up to 85 p.c. Ta_2O_5), *tapiolite* $Ta_2O_5\cdot Cb_2O_5\cdot FeO$ (up to 74 p.c. of Ta_2O_5), and other minerals containing widely varying proportions of Ta_2O_5, Cb_2O_5, FeO, and MnO. On reference to the article on TUNGSTEN, it will be seen that similar variations occur in the composition of wolfram, the tungstate of iron and manganese.

Tantalum also occurs as an apparently essential, although highly variable, constituent of between thirty and forty other minerals, including *microlite* $Ta_2O_5(CaO)_2$, containing up to about 70 p.c. of Ta_2O_5; *fergusonite*, a tantalate and columbate of yttrium, erbium, cerium, &c. (up to 43 p.c. Ta_2O_5); *yttrotantalite*, a tantalate and columbate of various rare earths (up to 47 p.c. Ta_2O_5); and *stibiotantalite*, a tantalate and columbate of antimony (up to 51 p.c. Ta_2O_5).

The principal localities where tantalum minerals occur have been detailed in the article on COLUMBIUM. At the present time, the main supply is obtained from Greenbushes, Pilbara, Wodgina, and elsewhere in Western Australia, where it occurs with tinstone and wolfram, partly in isolated masses which have escaped denudation during the weathering of the surrounding rocks, and largely in the form of alluvial material.

Metallic tantalum may be prepared in an impure state by reducing potassium tantalofluoride with potassium or sodium, or by reducing the pentoxide in the electric furnace with carbon. It was first prepared in a pure state by von Bolton, by reducing the tantalo-fluoride ($TaF_5\cdot 2KF$) with sodium and melting the washed, impure powder *in vacuó* in the electric furnace. The manufacture of the metal is entirely in the hands of Messrs. Siemens and Halske, and the exact present procedure is not known, but appears to be carried out according to von Bolton's method, the fusion *in vacuó* in the electric furnace being repeated with modification to remove all traces of impurity, and the preparation of the tantalo-fluoride being so conducted as to ensure its purity and freedom from columbium. The fusion *in vacuó* removes all traces of occluded gases, including the hydrogen and the oxygen (in the form of gas and of oxide) produced by the oxidation of the crude metal during the washing.

Another method devised by von Bolton consists in passing an electric current through rods of tantalum tetroxide Ta_2O_4 *in vacuô*. The intense heat produced by the current results in the expulsion of the oxygen and the production of brittle rods of impure metal which may be converted into pure tantalum by fusing and re-fusing *in vacuô* in the electric furnace as above. The tantalum tetroxide is prepared by shaping rods from a paste made of tantalum pentoxide and paraffin, and calcining them. The resultant metal possesses the same qualities as that made from the tantalo-fluoride, but the method is not employed on a commercial scale.

Wrought tantalum is a white metal, somewhat less bright than platinum, and usually showing a bluish tarnish from superficial oxidation. It has a sp.gr. of 16·8 (von Bolton); a specific heat, between 14° and 100°, of 0·033 (Dewar); and a m.p. of 2250°–2300° (von Bolton); 2798° according to tests made in 1912 at the University of Wisconsin. Its linear thermal coefficient of expansion between 0° and 60° is 0·0000079 according to tests made by the Imperial Standards Committee. It is about as hard as soft steel, but possesses a greater strength, the drawn wire having a tensile strength of 93 kilos per sq. mm. as against 80 kilos for good steel.

Tantalum is more malleable and ductile than columbium. It becomes progressively softer when heated, and can be hammered, rolled, or drawn into wire or seamless tubes similarly to steel, and is readily worked at a red heat. When heated in air, powdered tantalum readily oxidises, and both powder and thin wire burn at a red heat, the former with incandescence. Sheets of tantalum acquire a yellow tarnish at about 400° and, slowly at 500° or rapidly at 600°, become bluish, as in the case of steel when being tempered.

The worked metal possesses an extraordinary combination of toughness and hardness, and the slight superficial oxidation which is produced during working or by heating, enormously increases its property of resisting abrasion. So much is this the case that a diamond drill has but little penetrative power, although the metal is still capable of being rolled or drawn; the specially prepared metal has been found effective for the manufacture of pen nibs in place of iridium-pointed pens.

At a dull red heat, tantalum absorbs large quantities of hydrogen or nitrogen. At a yellow heat, about 740 volumes of hydrogen are thus absorbed. The metal is rendered brittle and fragile by the presence of either gas, but both can be expelled *in vacuô*. Three-fourths of the hydrogen can be driven off by heating to redness *in vacuô*, but the remainder can only be expelled by fusing *in vacuô* in the electric furnace, a treatment to which all metal now made is exposed, with a view to expelling all occluded gases and such other impurities as are volatile at the temperature at which tantalum melts.

The presence of occluded gases or small quantities of impurities completely alters the character of the metal, the value of which for all purposes to which it can be applied *as metal*, depends entirely on the extreme care taken in its purification after the preliminary stages of manufacture. The presence of even less than 0·1 p.c. of carbon renders it brittle, and it may be mentioned that the brittle metal obtained by Moissan in the electric furnace contained 0·5 p.c. The metallic nitride TaN, first prepared by Rose, is metallic in appearance, and was thought by him to be the metal itself.

Wrought tantalum is peculiarly resistant to all acids except hydrofluoric acid. It is absolutely unattacked by *aqua regia* even with prolonged boiling, and is not affected by organic acids or by the healthy or morbid secretions of the body, so that it is highly suited for the manufacture of dental and surgical instruments. Its extreme hardness permits of its use in place of steel, and the absence of corrosion and consequent ease of cleansing are resulting in an increased demand for such purposes.

Tantalum is readily attacked by fused caustic alkalis or alkaline nitrates and by sulphur. It alloys with iron, tungsten, molybdenum, and many other metals, but none of the alloys are of commercial importance excepting ferro-tantalum.

Ferro-tantalum is commonly prepared by the direct reduction of tantalite in the electric furnace, and is used to a small, but apparently increasing, extent in steel manufacture, for purposes similar to those for which ferro-tungsten, ferro-molybdenum, and ferro-vanadium are employed. The alloy commonly contains up to 50 p.c. of tantalum and columbium, the proportion of the latter being comparatively low and depending upon the amount which was present in the original tantalite.

Although the total output of metallic tantalum is under 2 tons per annum, its importance is considerable, especially in connection with the electric-lighting industry. Tantalum was the first metal to be used in commercial quantities for the manufacture of filaments. Its value depends on its great electrical resistance and high melting-point, and upon the fact that it can be drawn down to extremely fine wire (less than 0·03 mm.). The National Electric Lamp Association of the United States, in 1910 employed nearly five million feet of tantalum wire weighing under 100 lbs., for the manufacture of filaments.

According to Messrs. Siemens and Halske, taking the normal type of electric filament lamp of 25 c.p. at 110 volts, the filament for a lamp measures 650 mm., and has a diameter of 0·05 mm., so that 45,000 lamps could be made from 1 kilo of wire. This number is now largely exceeded, as it has been found possible to considerably reduce the diameter of the wire.

The electrical resistance (cold) of tantalum wire is 0·165 ohm per metre length of 1 sq. mm. section. When loaded to 1·5 watt per candle, the resistance of the same wire rises to 0·830 ohm.

G. T. H

COMPOUNDS OF TANTALUM.

Tantalum tetroxide Ta_2O_4, a porous dark-grey mass which scratches glass, is formed when the pentoxide is heated with magnesium in a carbon crucible. When powdered it is dark brown. It is not attacked by acids, but with chlorine gives a white readily volatile sublimate containing 18·5 p.c. chlorine. When heated it burns forming the pentoxide (Smith and Maas, Zeitsch. anorg. Chem. 1894, 7, 96).

Tantalum pentoxide Ta_2O_5 occurs in nature as the various *tantalites*, from which it may be obtained by fusing the finely-powdered mineral with three times its weight of acid potassium sulphate. The mass is boiled with water, and the residue is digested with ammonium sulphide, thus removing tin and tungsten and converting iron into sulphide. The residue is then washed and boiled with dilute hydrochloric acid and filtered; the mass consisting of the hydroxides of tantalum and columbium, and of titanic acid and silica, is washed with boiling water, dissolved in hydrofluoric acid, filtered, and heated to remove silicon fluoride; potassium fluoride is added to the solution which is then concentrated. The potassium tantalofluoride separates first; it is well washed, recrystallised, and heated to 400° with its own weight of concentrated sulphuric acid. The residue when boiled out with water gives the oxide and sulphuric acid. The acid adhering to the oxide may be removed from the oxide by heating with ammonium carbonate (Krüss and Nilson, Ber. 1887, 20, 1676; Moissan, Compt. rend. 1902, 134, 212). A more complete separation, which may be used for the estimation of tantalum, is described by Weiss and Landecker. The substance is fused with alkali bisulphite and the mass lixiviated with water. The solution is treated with sulphurous acid and boiled, when the tantalic, columbic, and titanic acids are precipitated quantitatively together with some tin, if present. The latter is removed by means of ammonium sulphide solution, and the residue is ignited and fused with a slight excess of sodium carbonate, and a small quantity of sodium nitrate is added towards the end of the operation, the mass being then gently heated until the nitrate is decomposed. The product is boiled with water and filtered from the titanium compound. After removing small quantities of the latter still present in the solution, it is treated with carbon dioxide or with a bicarbonate, whereby tantalic acid is precipitated quantitatively and, when heated to low redness, yields the pentoxide (D. R. P. 221429; J. Soc. Chem. Ind. 1910, 696; *see* also Zeitsch. anorg. Chem. 1909, 64, 65; Chesneau, Compt. rend. 1909, 149, 1132; also art. COLUMBIUM). Tantalum pentoxide is formed when the metal is treated with oxygen (Muthmann, Weiss and Riedelbauch, Annalen, 1907, 355, 58).

Tantalum pentoxide is a white amorphous, infusible powder, which, when strongly heated, becomes crystalline. It may also be obtained in rhombic prisms by igniting it with boron trioxide or melting it with microcosmic salt. Its sp.gr. varies with the intensity of the heat to which it has been subjected, and ranges from 7·055 to 8·257 (Marignac, Ann. Chim. Phys. 1866, [iv.] 9, 249). The ignited pentoxide is insoluble in acids, and is not acted on by hydrogen, but it may be reduced by heating strongly with carbon in the electric furnace. It forms double compounds with magnesium and the alkalis of the type $MgMTaO_8,xH_2O$ (M=alkali metal) (Balke and Smith, J. Amer. Chem. Soc. 1908, 30, 1637).

Tantalic acid $HTaO_3$ may be obtained as above or by mixing the chloride with water when it forms a gelatinous mass, which, when exposed to air, and then mixed with water containing ammonia, forms a crystalline powder. It is soluble in hydrofluoric, oxalic, and citric acids, but not in alkaline carbonates (Berzelius, Ann. Chim. Phys. [ii.] 3, 140).

Tantalates. For some naturally occurring tantalates and their extraction, *see* Rammelsberg, Chem. Soc. Trans. 1872, 25, 189. They are all insoluble, and are mostly derivatives of the above acid. In addition, *hexatantalates* are known of the formula $M_8Ta_6O_{19},xH_2O$, the alkali salts of which are soluble in water, and may be obtained by dissolving the acid in alkali hydroxide, or by fusing the pentoxide with the alkali hydroxide or carbonates. When tantalum pentoxide is ignited with the chlorides of calcium, magnesium and other metals, crystalline tantalates of these metals are formed (Joly, Compt. rend. 1875, 81, 266, 1266).

Pertantalic acid $HTaO_4,nH_2O$ is obtained by treating its potassium salt with dilute sulphuric acid. It is a white powder, fairly stable, decomposed only above 100°, but resembling percolumbic acid in other respects.

The *potassium salt* $K_3TaO_8,\frac{1}{2}H_2O$ is obtained by fusing tantalum pentoxide with potassium hydroxide, the mass is extracted with a little water, filtered, warmed with a little hydrogen peroxide, filtered, precipitated with alcohol, and the precipitate after washing with alcohol and ether, is treated with hydrogen peroxide and potassium hydroxide, and finally reprecipitated with alcohol. The corresponding sodium and barium salts, also the potassium calcium salt $KCaTaO_8,4\frac{1}{2}H_2O$, and the sodium salt

$$NaTaO_4,NaO{\cdot}TaO_4,13H_2O$$

have also been prepared by treating the corresponding tantalate with hydrogen peroxide (Melikoff and Pissarjewsky, Zeitsch. anorg. Chem. 1899, 20, 340; Balke, J. Amer. Chem. Soc. 1905, 27, 1155; Balke and Smith, *l.c.*).

Tantalum pentachloride $TaCl_5$, obtained by heating a mixture of the pentoxide and carbon in a current of chlorine, forms light yellow needles, m.p. 211°, b.p. 241·6°/753 mm., and volatilise at 144° (Deville and Troost, Compt. rend. 1867, 64, 294; *see* Willgerodt, J. pr. Chem. 1887, [ii.] 35, 391; Hermann, *ibid.* 1872, [ii.] 5, 66).

Tantalum pentabromide $TaBr_5$ can be prepared by passing bromine vapour over a strongly heated mixture of freshly-ignited tantalic oxide and pure sugar-carbon, air having been previously removed by heating the mixture in a current of dry carbon dioxide. It forms long yellow plates, m.p. about 240°, b.p. about 320°, fumes in moist air and reacts readily with methyl and ethyl alcohols.

Tantalum pentaiodide TaI_5 can be prepared by heating the bromide in a current of hydrogen iodide. It forms almost black plates, melts to a dark brown liquid, can be distilled in a current of carbon dioxide and fumes in moist air (van Haagen, J. Amer. Chem. Soc. 1910, 32, 729).

Bromotantalum bromide $(Ta_6Br_{12})Br_2,7H_2O$ has been obtained by reducing the pentabromide with sodium amalgam. It forms minute, black, hexagonal prisms giving a dark green powder. It is very stable and has tinctorial properties. A very minute quantity of the bromide is sufficient to give a beautiful emerald green colour to a considerable quantity of water and the solution imparts a stable pale-green colour to silk. Only two of the bromine atoms are in the ionic condition. When treated with caustic soda it is transformed into the *hydroxide* $(Ta_6Br_{12})(OH)_2,10H_2O$, thin hexagonal plates, which, on treatment with hydrochloric acid gives the *chloride*

$$(Ta_6Br_{12})Cl_2,7H_2O.$$

The *iodide* $(Ta_6Br_{12})I_2,7H_2O$ and the *chlorotantalum chloride* $(Ta_6Cl_{12})Cl_2,7H_2O$ have also been prepared (Chapin, J. Amer. Chem. Soc. 1910, 32, 323).

Tantalum pentafluoride TaF_5 is obtained by subjecting dry roughly powdered warmed tantalum contained in a boat inserted in a platinum tube, to the action of fluorine. The pentafluoride is purified by distilling it *in vacuô* at about 90°–100°. It forms colourless, strongly refractive prisms, m.p. 94° (corr.), b.p. 225°–226·5° (corr.), is very hygroscopic and is readily soluble in water. Caustic soda or ammonia precipitate tantalic acid containing a little fluorine from the solution. The fluoride attacks glass slowly at ordinary temperature, but rapidly when heated (Ruff, Zedner, Schiller, and Heinzelmann, Ber. 1909, 42, 492).

Tantalum pentafluoride forms a number of double fluorides with other metals (Balke, *l.c.* 1140; Smith, Chem. Zentr. 1905, ii. 1160; Ephraim and Heymann, Ber. 1909, 42, 4456), of which the

Potassium tantalofluoride $2KF,TaF_5$ is the most important. It is formed by bringing the two fluorides together in a dilute aqueous solution of hydrofluoric acid and consists of small anhydrous needles. On standing hydrofluoric acid is evolved. It is much more soluble in hot than in cold water, but when the solution is boiled an insoluble oxyfluoride $Ta_2O_5+2(2KF{\cdot}TaF_5)$ is precipitated (Krüss and Nilson, *l.c.*). The reactions of tantalum potassium fluoride are given in tabular form by Hall (J. Amer. Chem. Soc. 1904, 26, 1235). Tantalum pentafluoride also forms double salts with pyridine and other organic bases.

The following tantalum double salts with pyridine and quinoline have been prepared by the action of the base on an alcoholic solution of tantalum pentachloride containing hydrochloric acid

$$TaOCl_3,2C_5H_6NCl,2C_2H_6O\ ;$$
$$2TaOCl_3,3C_5H_6NCl,2C_2H_6O\ ;$$
$$Ta_2O_3Cl_4,4C_5H_6NCl\ ;\ \text{and}$$
$$TaOCl_3 2C_9H_8NCl,2C_2H_6O.$$

All these salts form colourless crystals soluble in alcohol, decomposed by water and becoming opaque on exposure to air (Weinland and Storz, Zeitsch. anorg. Chem. 1907, 54, 223).

Tantalum tetrasulphide Ta_2S_4 or TaS_2 may be prepared by passing a stream of sulphuretted hydrogen carrying carbon disulphide over tantalum pentoxide at 650°–900°. It is a very stable body not decomposed at 1300°, is scarcely attacked by boiling acids, readily absorbs moisture, and commences to be transformed into a crystalline variety at 1200° (Biltz and Kircher, Ber. 1910, 43, 1636).

Tantalum nitride Ta_3N_5 is obtained by heating the metal to 1000° in nitrogen (Muthmann, Weiss and Riedelbauch, Annalen, 1907, 355, 58), or by passing ammonia over tantalum chloride heated to a temperature not above that at which ammonium chloride volatilises. It is an amorphous yellowish-red mass, which, when heated to whiteness in dry ammonia forms the black *nitride* TaN (Joly, Compt. rend. 1876, 82, 1195).

Tantalum silicide $TaSi_2$ crystallises in iron-grey prisms, sp.gr. 8·83, with a metallic lustre; is decomposed readily by fused alkalis, dissolves in hydrofluoric acid, reacts with fluorine when heated gently, and is oxidised when heated in a current of oxygen (Hönigschmid, Monatsh. 1907, 28, 1017).

TAP CINDER. The basic iron silicate constituting the slag and flowing through the taphole of the puddling furnace, *v.* IRON.

TAPHOSOTE *v.* SYNTHETIC DRUGS.

TAPIOCA. A product obtained from the starch of cassava (*q.v.*) *Manihot utilissima* (Pohl) and other species of *Manihot.* The moist starch is heated and stirred until it agglutinates into little rounded, rugged masses, in which state it constitutes the tapioca of commerce. The starch granules become more or less swollen by this treatment, some of them preserving their original shape and character, while others gelatinise into shapeless or irregular masses. Tapioca usually contains from 10 to 14 p.c. of moisture with traces of nitrogenous matter and fat, but should be free from fibrous matter if properly prepared (Balland, J. Pharm. Chim. 1903, 17, 316).

The average of the analyses of seven samples of commercial tapioca (Bull. U. S. Dept. of Agric. 28, 1899) gave:

Water	Protein	Fat	N-free extract	Crude fibre	Ash
11·4	0·4	0·1	87·9	0·1	0·1

H. I.

TAR, WOOD, *v.* WOOD, DESTRUCTIVE DISTILLATION OF.

TARAXACERIN, TARAXACIN, TARAXACUM *v.* DANDELION ROOT.

TARRAGON OIL *v.* OILS, ESSENTIAL.

TARTAR *v.* TARTARIC ACID.

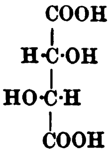
TARTAR, CREAM OF, *Potassium hydrogen tartrate v.* TARTARIC ACID.

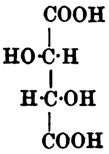
TARTAR EMETIC, *Potassium antimony tartrate v.* ANTIMONY.

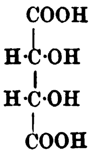
TARTARIC ACID, *Dihydroxysuccinic acid* (*Acide tartarique; Weinsaüre, Weinsteinsaüre, Tartarsaüre*), $C_4H_6O_6$.

The existence of the acid potassium salt of this acid in the deposit from fermented grape-juice was known to the Greeks and Romans, and the term 'tartarum' was applied to the deposit by Paracelsus, but it was generally considered to be an acid and to contain no base, although an alkali was known to be present in the ash. The production of an alkali by boiling tartar with lime was noticed by Kunkel in 1677, but the acid was not isolated until 1769, when Scheele obtained it by boiling tartar with chalk and decomposing the product with sulphuric acid.

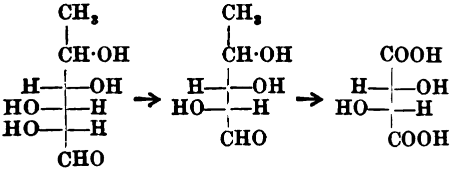
Tartaric acid contains two asymmetric carbon atoms and hence exists in four modifications, *viz.*: *d*-tartaric acid and *l*-tartaric acid which rotate the plane of polarised light to the right and left respectively; *r*-tartaric acid or racemic acid which is optically inactive, being a racemic mixture of the above two acids; *i*-tartaric acid or mesotartaric acid which is also optically inactive, as the lower half of the molecule is the mirror image of the upper half. Racemic acid is said to be 'externally compensated' and mesotartaric acid 'internally compensated.' The configurations of *d*-, *l*-, and *i*-tartaric acids are shown below :—


d-Acid.

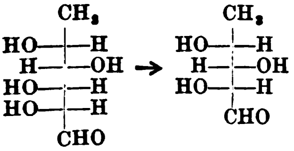

l-Acid.

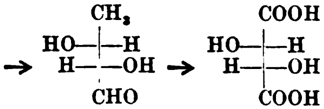

i-Acid.

The relative configuration of *d*- and *l*-tartaric acids to the sugars has been determined by Fischer (Ber. 1896, 29, 1377). The configuration of the *d*-acid was determined by converting rhamnose into rhamno-tetrose by the Wohl degradation and oxidising the methyl tetrose to *d*-tartaric acid with nitric acid.


d-Rhamnose. *d*-Rhamno-tetrose. *d*-Tartaric Acid.

Similarly the configuration of the *l*-acid was determined from *l*-gulose.


l-Gulose. *l*-Xylose.


l-Threose. *l*-Tartaric Acid.

Physico-chemical data.—The following table compares some of the constants of the four acids :—

—	M.p.	Sp.gr.	Mol. of water of cryst.	No. of grams dissolved by 100 grams H_2O.	Affinity constant.
d-Tartaric acid	168°–170°	1·755	—	132·2	0·097
l-Tartaric acid	168°–170°	1·754	—	132·2	0·007
r-Tartaric acid	205°–206°	1·697	1 H_2O	17·07	0·097
i-Tartaric acid	140°	1·666	1 H_2O	125·0	0·06

The specific gravity of solutions of *d*-tartaric and racemic acids of equal concentration are in close agreement up to concentrations of 10 p.c. Between concentrations of 10 p.c. and 14 p.c. the solution of racemic acid has a smaller specific volume than that of one of tartaric acid of the same concentration as shown in the following table :—

Percentage of acid in solution.	Sp.gr. of tartaric acid solution.	Sp.gr. of racemic acid solution.	Sp. vol. of tartaric acid solution (d_1).	Sp. vol. of racemic acid solution (d_2).	$d_1 - d_2$.
10·666	1·04950	1·04969	0·95283	0·95266	0·00017
14·018	1·06600	1·06623	0·93809	0·93788	0·00021

The specific gravities of 4 p.c. solutions of *d*- and *l*-tartaric acids are 1·01770 and 1·01767 respectively. On mixing the two solutions to obtain racemic acid the values obtained in two experiments were 1·01769 and 1·01766. Hence there is no change in specific gravity. All these values are compared with water at 4° and reduced to vacuum (Marchlewski, Ber. 1892, 25, 1556). According to Jahn (Wiedemann's Annalen, 1891, 43, 306) when *d*- and *l*-tartaric acids are mixed to give racemic acid, no heat is evolved. Also the heat of neutralisation of *d*- and *l*-tartaric acids by optically active bases is the same. The following data are given by Berthelot (Compt. rend. 1891, 112, 827). When solutions of the sodium salts of *d*- or *l*-tartaric acids are mixed with calcium chloride solution, at first heat is developed, but no precipitate is formed. After a few minutes a precipitate separates with a further development of heat. The values for *d*-tartaric acid are +0·98 Cals. and +2·68 Cals., and for *l*-tartaric acid +0·92 Cals. and +2·61 Cals. When the sodium salts of *d*- and *l*-tartaric acid are mixed to give sodium racemate, there is no development of heat. The heats of neutralisation of the four tartaric acids by sodium hydroxide are practically identical under similar conditions of temperature and concentration, *viz.* +12·7 Cals. per equivalent. The rates of diffusion of *d*- and *l*-tartaric acids are the same (Marchlewski, Ber. 1893, 26, 983). For relation between the optical activity and absorption spectra of the tartaric acids, *v.* Stewart, Chem. Soc. Trans. 1907, 1037.

Physiological action. According to Chabrié (Compt. rend. 1893, 116, 1410) the order of toxicity of the tartaric acids as determined by experiments on guinea pigs is *l*-tartaric acid, *d*-tartaric acid, racemic acid, and mesotartaric acid, the *l*- acid being twice as poisonous as the *d*- acid. Karczag examined the effect of the four acids on the cardio-inhibitory and vaso-motor centres and on the isolated cardiac and ventricle by intravenous injection (Zeitsch. Biol. 1909, 53, 218). On the cardio-inhibitory and vaso-motor centres, *l*-tartaric acid is the most reactive and *d*-tartaric acid the least, racemic and mesotartaric acids occupying intermediate positions. Mesotartaric acid has the least action on the isolated cardiac and ventricle. When dogs are fed with *d*- or *l*-tartaric acid or with racemic acid, the acids pass unchanged into the urine. Hence there is no evidence that *d*- or *l*-tartaric acids are consumed at different rates in the body (Neuberg and Saneyoshi, Biochem. Zeitsch. 1911, 36, 32). According to Brion, *l*-tartaric and mesotartaric acids are most completely oxidised in the organism of a dog, the *d*- acid much less so, and racemic acid least of all. Hence racemic acid is not resolved into *d*- and *l*-tartaric acids in its passage through the organism (Zeitsch. physiol. Chem. 1898, 25, 283).

More carbon dioxide is evolved in the earlier stages of the reaction between yeast and *d*-tartaric acid than is the case when *l*-tartaric acid is used. Racemic acid occupies an intermediate position, while mesotartaric acid acts similarly to *d*-tartaric acid (Karczag, Biochem. Zeitsch. 1912, 38, 516).

Separation of the tartaric acids. Holleman (Rec. trav. chim. 1898, 17, 66) has devised the following method for the separation of *d*-tartaric acid, racemic acid, and mesotartaric acid. The aqueous solution of the free acids is evaporated on the water-bath until crystallisation commences and the liquid is then left for 24 hours in a cool place. The racemic acid separates quantitatively and the crystals are carefully drained, dried, and weighed. The mother liquor is diluted to 20 c.c., and 10 c.c. of this are exactly neutralised with potassium hydroxide and the other 10 c.c. are added and the liquid is left overnight, when potassium hydrogen *d*-tartrate separates out and is filtered, washed with a very little water, dried and weighed. The filtrate is neutralised with ammonia, made slightly acid with acetic acid, boiled and treated with calcium chloride solution. After leaving for a further 24 hours the calcium mesotartrate, which has separated, is filtered, dried, and weighed.

d-TARTARIC ACID.

d-Tartaric acid has been obtained together with racemic acid by the oxidation of saccharic acid, dextrose, cane sugar, milk-sugar, starch, gum arabic and sorbin with nitric acid (Dessaignes, Annalen, Suppl. 2, 242; Hornemann, J. 1863, 38; Kiliani, Annalen, 1880, 205, 175). It can also be obtained by the resolution of racemic acid and its salts into their optical antipodes (*v. infra*). For asymmetric synthesis from *d*-bornyl fumarate by the action of potassium permanganate. *v.* McKenzie and Wren, Chem. Soc. Trans. 1907, 1215. According to Zinno tartaric acid can be synthesised by the following methods: (i.) by oxidising succinic acid in cold concentrated aqueous solution with hydrogen peroxide; (ii.) by oxidising calcium succinate with calcium hypochlorite; (iii.) by treating glyceric acid of 26° B. with a solution of potassium hydroxide of sp.gr. not greater than 1·134 at 15°, and finally with carbon dioxide under a pressure of 3 atmos., whereby cream of tartar is produced; (iv.) by heating *l*-malic acid with hydrogen peroxide at 120°; if an ethereal solution of *l*-malic acid is used, a mixture of *d*-tartaric and racemic acids is obtained (Mon. Sci. 1902, 16, 493; L'Orosi, 1902, 25, 293).

Occurrence. Tartaric acid occurs in nature in the free state, or, more often, as the acid potassium salt and to a small extent as the calcium salt in association with oxalic, malic, citric, and probably racemic acid, in tamarinds, mulberries, sorrel, cucumbers, and many other plants. It occurs in large quantity in the juice of the grape, which furnishes practically all that is found in commerce. According to Winter (Zeitsch. ver. Rübenzucker Ind. 1888, 38, 380) it does not exist in the juice from the sugar-cane, but it is found in the precipitated calcium salts obtained in the treatment of beet juice (Lippmann, Ber. 1894, 24, 3299). Metzger states that tartaric acid is present in oak wood (Bied. Zentr. 1897, 26, 678). When tartaric acid is added to a solution containing potassium malate, succinate, pectinate, acetate, hydrogen sulphate, or hydrogen phosphate or a mixture of these salts, potassium hydrogen tartrate is always precipitated. Hence Carpené concludes that tartaric acid cannot exist in the free state in wines in the presence of these salts (Selmi, 1894, 4, 13).

A possible explanation of the occurrence of tartaric acid in nature has been given by Genvresse (Compt. rend. 1892, 114, 555). By the action of nascent hydrogen glyoxylic acid is converted into racemic acid. The former acid occurs in nature in unripe grapes, gooseberries, &c., and it may be that the tartaric acid is produced from the glyoxylic acid in an analogous manner.

When the grape juice ferments, the potassium hydrogen tartrate is gradually deposited, on account of its less solubility in the alcohol produced, partly as a crystalline crust on the sides of the vat and partly with the 'lees' which consists of yeast and the various suspended matters of the must. The crust is known as 'argol,' and when recrystallised produces 'tartar,' which by further crystallisation is converted into 'cream of tartar,' technically known as 'cream.'

The quality of lees, argol, and tartar varies enormously. Superior argols are equal to tartar, while inferior varieties are little better than lees. The tartaric acid in argols varies from 40–70 p.c., and that in lees averages about 25 p.c., but varies within wide limits. Lees from 'plastered wines,' *i.e.* from those in which baked gypsum or 'yeso' has been trodden with the grapes, as in Spain, Cyprus, and the Greek Islands, the Marsala district of Sicily, and the South of France, contain very little tartar, the acid being mostly present as the calcium salt.

The best class of coloured tartars consist of nearly pure potassium hydrogen tartrate. That of Messina usually contains 76 p.c. of tartaric acid, 1½–3½ p.c. of which is present as the calcium salt, whilst that from St. Antimo contains 74–75 p.c., of which the calcium salt constitutes 3–4½ p.c. Vinaccia tartar, which is obtained from the skins and solid matters of grapes, contains about 70–73 p.c. of tartaric acid, 5–7 p.c. being calcium salt. Occasionally much greater quantities of calcium tartrate are formed in crude tartar. The table (p. 405) shows the composition of tartars and lees from different localities (Warington, J. Soc. Arts. 1876, 370).

The following table shows the general composition of lees (Warington, *l.c.*):—

—	Tartaric acid as		Total tartaric acid.
	Potassium hydrogen tartrate.	Calcium tartrate.	
Italian (33 samples)	24·10	6·1	30·2
Greek (14 samples)	19·90	11·8	31·7
French (9 samples)	17·30	6·0	23·3
,, (30 samples)	5·30	20·5	25·8
Yellow Spanish (59 samples)	8·70	18·2	26·9
Red Spanish (17 samples)	8·80	17·4	26·2

—	Messina tartar.	St. Antimo tartar.	French lees (plastered).	Spanish lees (plastered).	Spanish lees (unplastered).
Tartaric acid as acid tartrate	74·05	69·34	4·48	5·27	22·66
Tartaric acid as neutral tartrates	2·60	4·66	21·34	19·13	11·67
Tartaric anhydride	67·408	65·120	22·721	21·472	30·210
Sand	0·140	0·425	4·600	4·900	4·730
Silica	0·055	0·130	2·130	1·960	
Ferric oxide	0·053	0·086	0·394	0·351	0·214
Alumina	0·021	0·092	0·844	0·832	0·578
Phosphoric anhydride	0·041	0·068	0·527	0·486	0·569
Lime	1·081	1·778	10·567	10·600	4·514
Magnesia	0·025	0·041	0·327	0·363	0·209
Potash	23·236	21·773	1·868	2·123	7·115
Soda	—	—	0·100	0·060	—
Sulphuric anhydride	—	—	4·566	5·729	—
Carbon dioxide	—	—	0·435	0·388	—
Chlorine	—	—	0·040	0·042	—
Combined water	5·688	6·396	5·904	5·552	4·159
Water at 100°, with vegetable and undetermined matter	2·252	4·091	—	—	—
Water at 100°	—	—	11·305	10·694	9·750
Vegetable matter	—	—	33·672	34·448	37·952
	100·000	100 000	100·000	100·000	100·000

The lees often contain calcium carbonate; also Spanish earth (a native aluminium magnesium silicate used in fining wine); gypsum when the wine has been plastered therewith; a resin when obtained from the Greek Islands. The vegetable matter contains considerable quantities of nitrogen. The lees are used for the manufacture of tartaric acid, either in the moist condition or after being dried. The moist pasty lees are removed from tuns into sacks and pressed. They contain varying amounts of potassium hydrogen tartrate and calcium tartrate with some alcohol and higher esters. They are mixed with water and distilled, the distillate yielding the so-called Lager brandy and wine oil or Cognac oil. The residue, which is used for the manufacture of tartaric acid, contains from 1–8 p.c. of the acid. Lees containing a higher percentage of tartaric acid, which only occurs after the first stage of the fermentation, are well pressed and dried, usually by the heat of the sun, and sold as dried wine lees.

Preparation and manufacture. Scheele's process for preparing the acid consisted in merely neutralising the solution of the tartar with chalk, and decomposing the precipitated tartar with sulphuric acid. By this process, however, only half the acid was extracted, the rest remaining in solution as potassium tartrate:—

$$2C_4H_5O_6K+CaCO_3$$
$$=C_4H_4O_6K_2+C_4H_4O_6Ca+H_2O+CO_2.$$

The first improvement on this process consisted in the replacement of chalk by lime, which produced a larger yield although a portion of the calcium tartrate was retained in solution by the potassium hydroxide produced. Lowitz next suggested the precipitation of the residual tartrate from the solution, after the treatment with chalk, by addition of calcium chloride (Aitkin's Dict. of Chemistry, 1807, ii. 405). This was in turn superseded by a process attributed to Desfosses, and consisting in the replacement of the calcium chloride by the precipitated calcium sulphate obtained by treatment of calcium tartrate with sulphuric acid.

The methods in use vary according to the nature of the crude material. A suitable mode of procedure in the case of an argol is to mix the powdered argol with water, add hydrochloric acid and boil (4–5 cub. metres of water and 110–120 kilos. of crude hydrochloric acid of 20°–22°B. with 500 kilos. of argol). The solution is nearly neutralised with milk of lime, whereby calcium tartrate is precipitated and potassium tartrate and calcium chloride remain in solution. The potassium tartrate is decomposed either by boiling with a sufficient quantity of calcium sulphate or by adding calcium chloride solution, an excess of the precipitant being avoided in either case. The small amount of potassium hydrogen tartrate purposely left in the liquid, when treating the latter with milk of lime, is decomposed with pure precipitated calcium carbonate. The object of not adding sufficient milk of lime to neutralise the solution is to avoid the precipitation of iron oxide and alumina. The liquid must still remain slightly acid after the addition of the calcium carbonate. After cooling to about 40°C. the liquid is filtered off with the aid of a suction pump and the residue washed with water. The calcium tartrate is then mixed with water and decomposed with dilute sulphuric acid, a portion of the solution being tested at intervals to ascertain when sufficient acid has been added; the reagent employed is calcium chloride, which gives no precipitate with the calcium sulphate contained in the solution, but precipitates the free acid.

The gypsum resulting from the decomposition is washed on a vacuum filter, and the liquors are evaporated in steam-heated leaden pans, or in vacuum pans. After partial concentration the liquor is run off from the gypsum which has deposited on the sides of the pan, and is concentrated to the crystallising-point, when it is run into a tub and continuously agitated by a mechanical stirrer to produce a granular 'salt.' This system of crystallisation separates the salt in about a fifth of the time required for crystallisation by standing. The mother-liquor from the 'salt' is concentrated and a second and third crop of crystals are obtained by 'granulation' as above; the residual dark-coloured impure solution is known as 'old liquor.' The granular salt is re-dissolved, heated with animal charcoal which has been freed from calcium phosphate by digestion with hydrochloric acid; the solution is filtered, concentrated, and crystallised in cylindrical leaden pans about 2 feet deep. Tartaric acid thus prepared always contains lead. The crystallisation is assisted by the addition of sulphuric acid, in which the acid is less soluble than in water (*v. infra*).

The mother-liquors are diluted and precipitated with milk of lime, and thus produce a further quantity of calcium tartrate, which is worked up as above. It is found, however, that the iron, alumina, and phosphoric acid introduced in the tartar, charcoal, whiting, &c., gradually accumulate in the liquors, and greatly reduce their power of crystallising so that continuously more and more sulphuric acid must be added to induce crystallisation. According to Carles (Bull. Soc. chim. 1910, [iv.] 7, 326) the iron may be removed by precipitation with potassium ferrocyanide and filtration, when crystallisation is much facilitated. The old liquor finally becomes thick and yields no tartaric acid, although a considerable quantity remains in solution, together with a large amount of decomposition products, principally due to the action of the sulphuric acid. A process has been patented for obtaining the potassium salts which are present in the calcium tartrate mother-liquors (Alberti, Fr. Pat. 402925; J. Soc. Chem. Ind. 1909, 1313).

The manufacture of tartaric acid from lees and low argols may be carried out by Scheurer-Kestner's process which consists in dissolving the lees, &c., in hydrochloric acid, which separates it from most of the organic impurities and colouring matter. The solution is precipitated by whiting or lime and treated as above (Scheurer-Kestner, Wurtz, Dict. of Chem. iii. 263). This extraction, however, is incomplete. If the filtration of the lees is attempted, the pores of the filter become clogged and even under a pressure of four or five atmospheres no liquid will pass through. Dietrich and Schnitzer overcame this difficulty by heating the lees under a pressure of 4 or 5 atmospheres for 6 hours, whereby the albuminoid substances are coagulated. Wet lees, when thus treated, can be readily filtered. Dried lees or argols are crushed, stirred in a tank with water, and heated by steam for half an hour, and then transferred to the pressure boiler. The lees are then treated with the requisite quantity of hydrochloric acid (21°–22°B.), filtered, pressed, and washed. The tartaric acid is precipitated with lime and calcium carbonate and the remaining operations are the same as in the treatment of argols with the exception that there is no need to add calcium chloride or sulphate.

Many modifications of the above processes have been patented. J. B. Lawes & Co. mix chalk and lime with a 27–35 p.c. solution of anhydrous calcium chloride and stir the tartar into the mixture. The amount of calcium chloride used should be greater than that of the chalk and the lime, and after the tartar has been added the chalk and lime should be in slight excess. After settling, the liquid is again treated with the calcium chloride mixture. The solid residue is decomposed with sulphuric acid in the usual manner (Eng. Pat. 11694; J. Soc. Chem. Ind. 1910, 1488). Schmitz and Toenges boil argols or crude tartars with slight excess of alkali carbonate and treat the warm lye with sodium hypochlorite until the colour has changed from brown to light yellow. The solution is neutralised with acetic or hydrochloric acid and the tartaric acid is precipitated with calcium chloride. The calcium tartrate thus obtained is boiled with alkali carbonate and treated as above. If cream of tartar is required, after boiling the calcium tartrate with potassium carbonate, the calcium carbonate is filtered off and a suitable acid added to precipitate the cream of tartar (Eng. Pat. 21178; *ibid.* 1897, 799). Another process, whereby a saving of 50 p.c. in reagents is claimed, consists in dividing the crude material into two parts and treating one portion with alkali and the other with acid. To the acid portion is added an amount of oxalic acid equivalent to the calcium salts present and to the alkali portion potassium chloride or other potassium salt, so that on mixing the two solutions all the tartaric acid is precipitated as potassium hydrogen tartrate and all the calcium salts as calcium oxalate. The precipitate, after being filtered, is treated with hot water containing a small quantity of oxalic acid and on filtering and cooling the solution, potassium hydrogen tartrate separates out. The oxalic acid can be recovered and used again (Cantoni, Chautemo et Cie et Degrange, Fr. Pat. 426714; *ibid.* 1911, 956). Another method, having the same object in view, is that of Moszczenski (U.S. Pat. 1000433; *ibid.* 1911, 1115). The crude material is made into a paste with water and lime is added, whereby potassium tartrate is formed in solution, leaving calcium tartrate in the residue. The liquid is filtered off and tartaric acid obtained from the residue by the addition of sulphuric acid. On mixing the two solutions, potassium hydrogen tartrate is precipitated. Perigny and Mazet treat the crude material electrolytically and by the use of suitable anodes, obtain metallic tartrates. The yield is improved by esterifying one or both of the alcoholic hydroxyl groups with boric or antimonious acid and subsequently hydrolysing the product (Fr. Pat. 382824; *ibid.* 1908, 296, 470).

Methods for the treatment of lees have been patented by Auzies, Secheyron and Subra (Fr. Pat. 429008; *ibid.* 1911, 1253), and by Martignier and Montpellier (Eng. Pat. 20078; *ibid.* 1891, 253). The former add sulphuric acid to the lees and sufficient hot water to dissolve the potassium sulphate and tartaric acid thus formed. On cooling the potassium sulphate separates out and the tartaric acid may be obtained from the mother-liquors by concentration and crystallisation. If much pectic substance is present the tartaric acid is best obtained by dialysis. The latter neutralise the lees and add an excess of a saturated solution of potassium sulphate, calcium sulphate being precipitated, and potassium tartrate going into solution. The filtered solution is decolorised with animal charcoal and sulphuric acid added to precipitate the potassium hydrogen tartrate.

If grape marcs form the crude material, they are usually only pressed or extracted with hot water, since after this treatment they can be sold as fodder for cattle, whereas if acid has been used, they become valueless for this purpose (Janson, Chem. Ind. 1909, 32, 719). Most processes for utilising grape marcs as a source of tartaric acid also aim at recovering the alcohol they contain. Salat extracts the marcs with water or with a liquid which has previously been obtained in the process. Sufficient sulphuric acid is added to the extract to decompose all calcium tartrate, and enough oxalic acid to dissolve all the potassium hydrogen tartrate. After 6 hours the alcohol is distilled off and the residual liquid is treated, while hot, with enough potassium sulphate to convert all the tartaric acid into potassium hydrogen tartrate and immediately afterwards with sufficient lime or chalk to neutralise the sulphuric and oxalic acids. After standing for 30 minutes the liquid is filtered and potassium hydrogen tartrate separates from the filtrate on cooling (Fr. Pat. 421730; *ibid.* 1911, 441). Barbet lixiviates the marcs in a battery with water made alkaline with sodium carbonate. To the extract is added an amount of sulphuric acid exactly equivalent to the sodium carbonate used. After a few days the liquid is filtered and the alcohol distilled off. The cream of tartar is then obtained as such by evaporation or as calcium tartrate by precipitation with calcium chloride (Fr. Pat. 379038; *ibid.* 1907, 1211). Ciapetti charges a series of diffusion vessels with the marcs, drives off the alcohol by steam and then acts on them with an aqueous solution of sulphurous acid under pressure. This treatment decolorises the solution and gives potassium hydrogen sulphite and tartaric acid in solution. After this solution has passed through the series of vessels, it is heated to 80°, whereby sulphur dioxide is expelled and cream of tartar is precipitated (Fr. Pat. 330951; *ibid.* 1903, 1099). Jude dissolves out the tartaric acid by the addition of an acid to the marcs and treats the filtrate with a potassium salt, such as the chloride, and a carbonate in quick succession so as to obtain a precipitate rich in potassium hydrogen tartrate (Fr. Pat. 402999; *ibid.* 1909, 1326; *cf.* Carles, Fr. Pat. 365034; *ibid.* 1906, 952).

A preliminary treatment of the crude material to render the colouring matters which are present insoluble, forms the subject of several patents. The crude lye may be boiled for 45 minutes after treatment with formalin (*ibid.* 1909, 913); if the proportion of albuminous material in the lye is low, blood, white of egg, casein or glue, &c., is added and then formalin and the substance taken to dryness at 140° (Garin and David, Fr. Pat. 374276; *ibid.* 1908, 712). Crude tartrates are treated with 1–2 p.c. of formalin or trioxymethylene and dried; the liquids obtained subsequently by extraction have very little colour (Garin, Annemasse and David, Fr. Pat. 8375; *ibid.* 1907, 778). Faucheux and Boissière submit the crude material to a slight roasting by means of hot gases from a furnace, whereby all organic matter other than tartrates is decomposed and the iron and aluminium compounds which are present, are rendered insoluble (Fr. Pat. 338735; *ibid.* 1904, 680). Vigneaux adds acid to the crude material and then zinc or some other metal to remove the excess of the acid, the hydrogen evolved decolorising the liquid. When the acid has been neutralised, potassium hydrogen tartrate is first deposited and finally calcium tartrate (Fr. Pat. 430883; Eng. Pat. 11558; *ibid.* 1911, 1382).

Fermaud extracts the crude substance with a hot solution of aluminium chloride or nitrate and claims thereby to get a purer product (D. R. P. 247452; *ibid.* 1912, 773). Special boilers for extracting the crude material have been patented by Roux (Eng. Pat. 7363; Fr. Pat. 328713; *ibid.* 1903, 1014) and Chauvin (Fr. Pat. 385103; *ibid.* 1908, 591). Cornette and Faucheux have patented a process for centrifugating out the potassium hydrogen tartrate after extracting the crude material with water (Eng. Pat. 5759; Fr. Pat. 435915; *ibid.* 1912, 386, 1125).

Other sources of tartaric acid than the grape have been proposed. Brehier and Talbot treat cellulose, saccharic or amylaceous substances with alkaline permanganate in the presence of chlorine. The nascent oxygen reacts on the glucose bodies and a tartaric acid liquor is produced from which the tartaric acid may be obtained by the usual methods (Eng. Pat. 3240; *ibid.* 1891, 751). Ellis treats a solution of a saccharic substance electrolytically and by anodic oxidation in the presence of substances yielding insoluble compounds with tartaric acid, obtains insoluble tartrates which are immediately removed from the field of oxidation (U.S. Pat. 789269; *ibid.* 1905, 635).

The crude tartrates obtained by any of these methods may be further purified by one of the following methods. Scarlata decomposes them with hydrofluosilicic acid yielding a residue of potassium fluosilicate while tartaric acid and calcium fluosilicate go into solution. After filtering, a slight excess of sulphuric acid is added to decompose the calcium fluosilicate and the precipitate of calcium sulphate having been removed, the tartaric acid is crystallised out (Mon. Sci. 1899, 783). Another method is to convert the crude tartrate into an alkali salt and add sulphuric acid. The filtered liquid is treated with aluminium sulphate in quantity sufficient to form an alum, and the latter is removed by evaporation and crystallisation. The tartaric acid is recovered from the mother liquors (Sir J. McDougall and F. L. McDougall, Eng. Pat. 4613; U.S. Pat. 898253; J. Soc. Chem. Ind. 1907, 1215). To obtain colourless cream of tartar, crude calcium tartrate is decomposed with sulphuric acid which has been freed from arsenic with sulphuretted hydrogen. After filtration the liquid is treated with purified animal charcoal and a small quantity of sodium thiosulphate, which prevents any iron or aluminium compounds being precipitated subsequently. After agitation the solution is again filtered and potassium carbonate added to precipitate the potassium hydrogen tartrate (Condouris and Tassopoulos, Fr. Pat. 366058; *ibid.* 1906, 1003; Tassopoulos, Eng. Pat. 16047; *ibid.* 1908, 876; *cf.* also Martignier, Eng. Pat. 27328; *ibid.* 1899, 1154).

Properties. Tartaric acid crystallises in large anhydrous monoclinic prisms having sp.gr. 1·755 (Walden, Ber. 1896, 29, 1701) and m.p. 168°–170° (Bischoff and Walden, *ibid.* 1889, 22, 1814). The crystals become luminous in the dark when rubbed. They often contain traces of lead owing to their having been crystallised in lead pans. The solubility of tartaric acid in water is given in the following table, the values being the same for *d*- and *l*-tartaric acids (Leide, Zeitsch. anal. Chem. 1883, 22, 269). The second column gives the number of parts of tartaric acid dissolved by 100 parts of water.

Temp.	Solubility	Temp.	Solubility
0°	115·04	55°	205·83
5°	120·0	60°	217·55
10°	125·72	65°	230·16
15°	132·20	70°	243·66
20°	139·44	75°	258·05
25°	147·44	80°	273·33
30°	156·20	85°	289·50
35°	165·72	90°	306·56
40°	176·0	95°	324·51
45°	185·06	100°	343·53
50°	195·0		

100 parts of 90 p.c. alcohol dissolve 29·146 parts of tartaric acid, whilst 100 parts of absolute alcohol at that temperature dissolve 20·385 parts (Bourgoin, Bull. Soc. chim. 1878, [ii.] 29, 244; *cf.* Schiff, Annalen, 1860, 113, 189). 100 parts of ether dissolve 0·393 part at 15° (Bourgoin, *l.c.*). A solution of tartaric acid saturated at 15° contains 57·9 parts of the acid (Gerlach, J. 1859, 44) or 57·75 parts (Maisch, *ibid.* 1865, 392). The table of specific gravities in the next column contains Gerlach's results (*cf.* Maisch, *l.c.*; Schiff, *l.c.*; Marchlewski, Ber. 1892, 25, 1560; Přibram and Glücksmann, Monatsh. 1898, 19, 123).

Strong solutions of tartaric acid contract on dilution. Thus 500 c.c. of a solution of sp.gr. 1·338 require 505·508 volumes of water to produce 1000 volumes (Warington, Journ. Chem. Soc. 1875, 942). The presence of much free sulphuric acid diminishes the solubility of tartaric acid at ordinary temperatures and increases the difference between the solubility at low and high temperatures. A cold saturated solution of tartaric acid, when mixed with half its volume of strong sulphuric acid and cooled, gives an abundant white precipitate of tartaric acid, whilst a hot solution of the acid in one volume of water and one and a half volumes of sulphuric acid (sp.gr. 1·713) deposits 70 p.c. of the tartaric acid on cooling. Thus a much larger proportion of tartaric acid is obtained in one crystallisation when sulphuric acid is present (Grosjean, Chem. Soc. Trans. 1883, 334).

Sp.gr. at 15°	Per cent. of acid in solution	Sp.gr. at 15°	Per cent. of acid in solution
1·0045	1	1·1505	30
1·0090	2	1·1560	31
1·0136	3	1·1615	32
1·0179	4	1·1670	33
1·0224	5	1·1726	34
1·0273	6	1·1781	35
1·0322	7	1·1840	36
1·0371	8	1·1900	37
1·0420	9	1·1959	38
1·0469	10	1·2019	39
1·0517	11	1·2078	40
1·0565	12	1·2138	41
1·0613	13	1·2198	42
1·0661	14	1·2259	43
1·0709	15	1·2317	44
1·0761	16	1·2377	45
1·0813	17	1·2441	46
1·0865	18	1·2504	47
1·0917	19	1·2568	48
1·0969	20	1·2632	49
1·1020	21	1·2696	50
1·1070	22	1·2762	51
1·1124	23	1·2828	52
1·1175	24	1·2894	53
1·1227	25	1·2961	54
1·1282	26	1·3027	55
1·1338	27	1·3093	56
1·1393	28	1·3159	57
1·1449	29	1·3220	57·9

The optical rotation $[\alpha]_D$ of aqueous solutions of the acid is given in the following table (Thomsen, J. pr. Chem. 1885, [ii.] 32, 318; *cf.* Kanonnikoff, J. Russ. Phys. Chem. Soc. 1890, 22, 369; Přibram and Glücksmann, *l.c.*).

Per cent. of acid	10°	15°	20°	25°	30°
50	5·93	6·67	7·38	8·03	8·64
40	7·58	8·26	8·91	9·51	10·07
30	9·22	9·85	10·45	10·99	11·50
20	10·87	11·44	11·98	12·47	12·93

In supersaturated aqueous solutions the rotation falls to 0°, and finally becomes lævorotatory (Lepeschkin, Ber. 1899, 32, 1180). In a mixture of dry ether and acetone the rotation is also lævorotatory (Landolt, *ibid.* 1880, 13, 2329). For rotation in solutions of ether and alcohol *v.* Přibram, Monatsh. 1888, 9, 488. According to Aignan tartaric acid exists in solution as the polymeride $(C_4H_6O_6)_2$ which is partially dissociated (Compt. rend. 1891, 112, 951). Affinity constant, k=0·097 (Walden, Ber. 1896, 29, 1701); dissociation constants, $k_1=970{\cdot}0\times10^{-6}$; $k_2=59{\cdot}0\times10^{-6}$ (Smith, Zeitsch. physikal. Chem. 1898, 25, 193). Molecular refraction *v.* Gladstone and Hibbert, Chem. Soc. Trans. 1897, 824. Conductivity *v.* Bischoff and Walden, *l.c.*; Ostwald, Zeitsch. physikal. Chem. 1889, 3, 371.

On heating tartaric acid at its melting-point some *ditartaric acid* is stated to be produced together with a variety of tartaric acid known as *metatartaric acid*. This acid is an amorphous deliquescent mass, the solution of which regenerates *d*-tartaric acid on boiling. It yields salts of greater solubility than the *d*-tartrates into which they are converted on boiling with water (Grosjean, Chem. Soc. Trans. 1883, 334; Erdmann, Annalen, 1837, 21, 9; Laurent and Gerhardt, *ibid.* 1849, 70, 348; Braconnot, Ann. Chim Phys. [ii.] 68, 299). By heating at 180°, or for a considerable time at 150°, *ditartaric acid* (*tartralic acid*) is obtained, while the further action of heat yields *tartrelic acid* (*soluble tartaric anhydride*) and *tartaric anhydride.* Ditartaric acid $C_8H_{10}O_{11}$ is an amorphous very deliquescent substance which readily combines with water, especially on boiling, to regenerate tartaric acid. Tartrelic acid $C_4H_4O_5$ forms yellow deliquescent crystals which are converted by boiling water first into ditartaric acid and then into tartaric acid. Tartaric anhydride $C_4H_4O_5$ is a colourless powder, insoluble in water, alcohol, or ether, but is converted by boiling water first into tartrelic acid, then into ditartaric acid and finally into tartaric acid (Warington, *l.c.*; Frémy, Annalen, 1839, 29, 444; Laurent and Gerhardt, Compt. rend. 1848, 27, 318; Schiff, Annalen, 1863, 125, 129).

The dry distillation of tartaric acid yields pyruvic acid, pyrotartaric acid, pyrotritaric acid, $C_7H_8O_7$, uvitic acid $C_7H_8O_3$, and acetic acid. These decompose yielding carbon monoxide, carbon dioxide, acetaldehyde, acetone, formic acid, and other compounds (Völckel, Annalen, 1854, 89, 57; Bourgoin, Bull. Soc. chim. 1878, [ii.] 29, 309; Pelouze, Ann. Chim. Phys. [ii.] 46, 297; Böttinger, Ber. 1876, 9, 670; Liebermann, *ibid.* 1882, 15, 428). Fusion with potassium hydroxide yields acetic and oxalic acids. By destructive distillation with potassium hydrogen sulphate an acid isomeric with pyrotritaric acid is obtained (Simon, Compt. rend. 1900, 131, 586). By heating tartaric acid with water, hydrochloric acid or alkali, racemic and mesotartaric acids are obtained in varying proportions (*v. Racemic acid, infra*). By oxidation with chromic acid, potassium permanganate or sulphuric acid, carbon dioxide and formic acid are obtained, whilst if slowly oxidised with nitric acid, tartronic acid is the product. Phosphorus and hydriodic acid reduce tartaric acid to malic and succinic acids. Phosphorus pentachloride yields chlorofumaric chloride.

By oxidising tartaric acid in the presence of a ferrous salt *dihydroxymaleic acid* $C_4H_4O_6,2H_2O$ is obtained. On reduction of the latter the final product is succinic acid, whilst on oxidation with glacial acetic acid and bromine *dihydroxytartaric acid* is produced, which is a good reagent for the detection of sodium salts (Fenton, Chem. Soc. Trans. 1895, 48; 1896, 546; 1898, 71, 472; Eng. Pat. 26259).

On exposure of a solution of tartaric acid to light for a year in a stoppered flask, Otto found that part was converted into pyruvic acid, although no micro-organisms were present (Ber. 1895, 27, 838, 1264). It is stated by Wehmer that a mould develops in pure tartaric acid solutions and is capable of existence in the presence of large amounts of acid. This mould produces citric acid fermentation in sugar solutions (Bied. Zentr. 1898, 27). On exposure of a 5 p.c. aqueous solution containing 1 p.c. uranium oxide to the action of sunlight, the first products are oxalic acid and a compound $C_2H_4O_2$ which reduces cupric salts. The oxalic acid is then converted into water, carbon dioxide and carbon monoxide and the last-named reduces part of the tartaric acid to malic acid and then to succinic acid. At the same time part of the malic acid is converted into oxalic acid and acetaldehyde and the succinic acid into propionic acid and carbon dioxide (Seekamp, Annalen, 1894, 278, 810).

Yeast ferments tartaric acid solutions yielding butyric and propionic acids, the latter being probably formed through the intermediate production of glyceric, malic, and succinic acids. Acetaldehyde is also present in small quantity (Karczag, Biochem. Zeitsch. 1912, 43, 44). On the purification of brewing yeast from wild yeasts by tartaric acid, *v.* Hansen, Zeitsch. Brauwesen, 1892, 2; Lindner, Wochenschrift Brauerei, 12, 316).

By the interaction of tartaric acid and trioxymethylene or formaldehyde under suitable conditions monomethylene- and dimethylene-tartaric acids can be obtained (Henneberg and Tollens, Annalen, 1896, 292, 53; van Ekenstein, Proc. K. Akad. Wetensch. Amsterdam, 1900, 3, 400; Rec. trav. chim. 1901, 20, 331; Sternberg, Pharm. Zeit. 1901, 46; Chem. Fabr. auf Aktien von E. Schering, D. R. P. 130346, Chem. Soc. Abstr. 1902, i. 705; de Bruyn and van Ekenstein, Rec. trav. chim. 1902, 21, 310). Tartaric acid gives a dinitrate in 81 p.c. yield on treatment with nitrogen pentoxide (Gibson, Proc. Roy. Soc. Edinburgh, 1908, 28, 705). When iron is placed in a solution of tartaric acid, hydrogen is evolved and the compound $C_4H_2O_6Fe_2$ is produced, showing that both the carboxylic and alcoholic hydrogen atoms have been replaced (Ulsch, Chem. Zeit. 1899, 23, 658).

Uses. Tartaric acid is used in certain photographical processes for printing and developing. It is also employed medicinally and for the production of baking powders, effervescent drinks, Seidlitz powders, &c. It is used by the calico printer to liberate chlorine from bleaching powder, and in the production of a number of dyestuffs; as a 'resist' for aluminium and other mordants and in the discharge colours for Turkey-red. It is also used in the mordant bath in dyeing wool; for brightening the colour of silk after dyeing; and for tendering cotton fibre.

Salts. Tartaric acid contains four hydrogen atoms which can be replaced by metals, but only two of these are in carboxyl groups, and hence the acid is dibasic forming two series of salts, the tartrates and the hydrogen tartrates or 'bitartrates.' Few of the salts are readily soluble in water and all are insoluble in alcohol.

Potassium hydrogen tartrate, cream of tartar, $C_4H_5O_6K$, occurs in the juice of the grape and is deposited on fermentation on account of its lesser solubility in alcohol, partly as a crystalline crust known as 'argol' and partly with the 'lees.' For composition of argol and lees *v.* pp. 404–405. The argol, &c., when heated with water, yields slightly coloured crystals of the purer salt which is known as 'tartar.' This may be further purified by any of the methods given under the manufacture of tartaric acid.

Potassium hydrogen tartrate crystallises in aggregates of small hard rhombic prisms, having a sp.gr. of 1·973 (Schiff, Annalen, 1859, 112, 89; *cf.* Schabus, J. 1850, 377; Buignet, *ibid.* 1861, 15; Cooke, *ibid.* 1880, 805). Its solubility in water and aqueous alcohol is given in the following table (Roelofsen, Amer. Chem. J. 1894, 16, 466; *cf.* Wenger, *ibid.* 1892, 14, 624; Blarez, Compt. rend. 1891, 112, 434, 808; Noyes and Clement, Zeitsch. physikal. Chem. 1894, 13, 413; Magnanini, Gazz. chim. ital. 1901, 31, ii. 542).

Temperature	Milligrams of $C_4H_5O_6K$ in 10 c.c.									
	Percentage of alcohol									Water
	90	80	70	60	50	40	30	20	10	
0°	6·2	6·4	4·9	6·0	6·0	6·2	7·0	10·8	17·3	30·1
5°	5·5	6·0	5·1	6·0	6·8	6·8	7·1	13·2	18·8	32·0
10°	6·2	6·2	5·1	5·8	6·4	7·0	8·6	16·0	27·0	41·1
15°	5·3	6·2	6·2	6·2	5·5	7·7	8·8	15·8	23·9	44·3
20°	6·4	6·4	6·2	6·4	7·0	9·6	11·3	17·1	29·3	49·0
25°	4·7	5·5	6·0	6·8	7·0	10·3	11·7	21·4	36·4	54·1
30°	4·7	6·0	6·8	7·5	8·5	11·0	13·1	24·8	39·9	69·2
35°	1·9	5·1	5·9	6·8	9·0	12·4	18·8	28·7	49·3	83·8
40°	1·7	5·3	5·8	7·0	10·2	14·9	23·1	37·7	53·6	95·9
45°	1·7	5·3	6·0	7·9	10·7	16·5	25·8	44·2	72·6	112·8
50°	1·5	5·1	6·0	8·1	12·8	19·0	29·7	53·6	87·2	124·8

The alteration of the solubility in water caused by the presence of other substances has been determined by Warington (Journ. Chem. Soc. 1875, 947; *cf.* Magnanini, *l.c.*; Noyes and Clement, *l.c.*; Blarez, *l.c.*). The following table gives the solubility at 14° in acid solutions of equal acidity, *i.e.* of such strength that equal volumes require the same amount of alkali for neutralisation; and in potassium acetate and citrate.

—	Grms. of acid or salt in 100 c.c.	Grms. of KHTa dissolved in 100 c.c.
Water . . .	—	0·422
Acetic acid . .	0·8106	0·422
Tartaric acid .	1·0331	0·322
Citric acid . .	0·8448	0·546
Sulphuric acid .	0·6853	1·701
Hydrochloric acid .	0·5037	1·949
Nitric acid . .	0·8445	1·969
Potassium acetate	1·3875	0·744
Potassium citrate .	1·3966	0·843

The solubility is thus diminished by the presence of tartaric acid and increased by the presence of other acids. These results are of great importance in the estimation of tartaric acid as potassium hydrogen tartrate. Mineral acids should not be present, nor any large excess of potassium acetate or citrate. The solubility of potassium hydrogen tartrate in water is greatly diminished if potassium sulphate, nitrate, or, especially, chloride be present. Grosjean showed that while the solubility in water at 12° was 1 in 262, the solubility in a 5 p.c. solution of potassium chloride was 1 in 3213, and in a 10 p.c. solution 1 in 4401. For conductivity of aqueous solutions, *v.* Walden, Zeitsch. physikal. Chem. 1891, 8, 466.

Potassium hydrogen tartrate has been proposed as a standard for acidimetry and alkalimetry (Bornträger, Zeitsch. anal. Chem. 1892, 31, 43; 1894, 33, 713; Zeitsch. angew. Chem. 1894, 54; Kollo, Pharm. Zentr-h. 1909, 50, 315; Hefelman, *ibid.* 334). To prepare pure potassium hydrogen tartrate for this purpose, white cream of tartar is heated with dilute hydrochloric acid, the solution cooled and stirred, and the precipitate filtered, washed, and recrystallised from hot water. Or a solution of tartaric acid may be divided into two equal parts, one portion being neutralised with potassium carbonate and the other portion added to it. The precipitate is washed and recrystallised from hot water. It is quite pure when the alkali obtained by calcining a weighed quantity exactly neutralises an equal weight of the uncalcined substance, neutral litmus paper being used as an indicator.

When heated, potassium hydrogen tartrate yields a mixture of carbon and potassium carbonate used as a reducing agent under the name of 'black flux.' Potassium hydrogen tartrate is used in the preparation of effervescing drinks, baking powders, &c., and in medicine; also in the mordant bath for wool dyeing, in conjunction with alum, iron salts, stannous chloride, &c., apparently producing double salts which are more effective as mordants.

Cream of tartar dissolves readily in a solution of boric acid or borax (Le Fèvre, Mémoires de L'Acad. Royale, Paris, 1732), and the product is used medicinally under the name 'soluble cream of tartar.' It is best prepared by dissolving a mixture of 4 parts of cream of tartar and 1 of boric acid in 24 parts of water and heating until most of the water is driven off. The salt prepared with boric acid is a white powder, which is permanent in the air, whereas that prepared with borax, and known in the German Pharmacopœia as 'Boraxweinstein' is deliquescent.

Potassium hydrogen tartrate dissolves many oxides, forming double tartrates; tartar emetic is a compound of this nature (*v.* ANTIMONY). Other double salts which have been prepared in a similar manner are the *titanitartrates* and *stannitartrates* (Henderson, Orr and Whitehead, Chem. Soc. Trans. 1899, 556; *cf.* Rosenheim and Schütte, Zeitsch. anorg. Chem. 1901, 26, 239); *molybdotartrates* (Henderson and Barr, Chem. Soc. Trans. 1896, 1455; *cf.* Rosenheim and Itzig, Ber. 1900, 33, 707; Itzig, *ibid.* 1901, 34, 1372); *glucinotartrates* (Rosenheim and Woge, Zeitsch. anorg. Chem. 1897, 15, 299); *tartrarsenites* (Henderson and Ewing, Chem. Soc. Trans. 1895, 103). The *tungstotarates* are prepared by boiling tungstic acid in a solution of a normal alkali tartrate (Rosenheim and Itzig *l.c.*).

Potassium ferric tartrate is prepared by adding precipitated ferric hydroxide to potassium hydrogen tartrate and treating with cold water. It is the *ferrum tartaratum* of pharmacy, and should yield 30 p.c. of Fe_2O_3 on ignition, as estimated from the weight of ash insoluble in water. It forms ruby-red transparent scales soluble in about 4 parts of water.

Potassium tartrate $C_4H_4O_6K_2,\frac{1}{2}H_2O$ is prepared by neutralising potassium hydrogen tartrate with potassium carbonate or hydroxide. It forms colourless, monoclinic crystals, which have sp.gr. 1·973 (Schiff, Annalen, 1859, 112, 89) and are soluble in 66 parts of water at 14°, the solubility decreasing with rise of temperature. When a solution of this salt is treated with acid, potassium hydrogen tartrate is precipitated. By the electrolysis of a concentrated aqueous solution of potassium tartrate potassium hydrogen tartrate, carbon dioxide, carbon monoxide, a little formaldehyde and formic acid, but no acetic acid are produced (Miller and Hofer, Ber. 1894, 27, 468).

Sodium hydrogen tartrate $C_4H_5O_6Na,H_2O$ and *sodium tartrate* $C_4H_4O_6Na_2,2H_2O$ crystallise in rhombic crystals (Dumas and Piria, Annalen, 1844, 44, 88). They are both very soluble; the normal salt dissolves in 2·28 parts of water at 24°, and the sp.gr. of the crystals is 1·794.

Potassium sodium tartrate, Rochelle salt $C_4H_4O_6NaK,4H_2O$ is prepared by neutralising potassium hydrogen tartrate with sodium carbonate or hydroxide. It forms large rhombic prisms of sp.gr. 1·767 (Schiff, *l.c*), and is soluble in 1·70 parts of water at 6° (Fresenius, Annalen, 1845, 53, 234). Above 40° a saturated solution deposits crystals of Rochelle salt and sodium tartrate, and above 55° a mixture of potassium and sodium tartrates (van Leeuwen, Zeitsch. physikal. Chem. 1897, 23, 33). Addition of acetic acid to the solution precipitates potassium hydrogen tartrate, this reaction distinguishing Rochelle salt from sodium tartrate. Seidlitz powders contain Rochelle salt, which is sometimes replaced wholly or partly by sodium hydrogen carbonate. Some powders also contain about 0·001 grain of tartar emetic.

Ammonium hydrogen tartrate $C_4H_5O_6NH_4$ and *ammonium tartrate* $C_4H_4O_6(NH_4)_2$ have similar properties to those of the corresponding potassium salts (Pasteur, J. 1853, 415; 1854, 395; Schiff, *l.c.*). *Ammonium potassium tartrate* $C_4H_4O_6K(NH_4)$ and *ammonium sodium tartrate* $C_4H_4O_6Na(NH_4),4H_2O$ resemble Rochelle salt in their properties.

Ammonium ferric tartrate, which is employed in medicine, is prepared according to the U.S. Dispensatory, 14th ed., p. 1214, by dissolving 6 oz. of tartaric acid in 2 pints of water and neutralising it with ammonium carbonate, 6 oz. of tartaric acid being then added. Ferric hydroxide, precipitated from a solution of ferric chloride, is then stirred in at 140°F. until no more will dissolve. The solution is then filtered, evaporated to a syrup at a temperature below 140°F. and dried on a glass plate. It forms transparent garnet-red scales of sweetish taste, which are slowly but extremely soluble in water to a neutral solution, but insoluble in alcohol or ether.

The normal and acid tartrates of *lithium, caesium,* and *rubidium* are all readily soluble. The rubidium salt crystallises from aqueous solutions in anhydrous, hexagonal, trapezohedral crystals, having sp.gr. 2·694 at 14°; they are lævorotatory (Traube, Sitzungsber. Berl. Akad. 1895, 10, 195).

Magnesium tartrate $C_4H_4O_6Mg,4H_2O$ is obtained as a crystalline crust by evaporating a solution of magnesium carbonate in tartaric acid, and is soluble in 123 parts of water at 15·6°. The acid salt $(C_4H_5O_6)_2Mg$ is obtained by dissolving magnesium carbonate in excess of tartaric acid. It is a crystalline substance, soluble in 53 parts of water at 15·6°. Double salts with the alkali metals are known.

Calcium tartrate $C_4H_4O_6Ca,4H_2O$ occurs in small quantities, together with the acid potassium salt, in many plants and is always found in argol and lees as described previously. It may be prepared by adding excess of calcium chloride to a solution of a tartrate. It crystallises in rhombic prisms or pyramids, but is frequently deposited from dilute solutions in aggregates of fine radiating needles, which gradually become converted into isolated pyramids or prisms. The solubilities of the tartrates of calcium, strontium, and barium are given in the following table (Cantoni and Zachovers, Bull. Soc. chim. 1904, [iii.] 31, 1121; *cf.* Enell, Zeitsch. anal. Chem. 1899, 38, 368):—

Temp.	Grms. of salt in 100 c.c. water		
	$C_4H_4O_6Ca,4H_2O$	$C_4H_4O_6Sr,3H_2O$	$C_4H_4O_6Ba$
0°	0·0365	0·112	0·0205
10°	0·0401	0·149	0·0242
20°	0·0475	0·200	0·0279
25°	0·0525	0·224	0·0297
30°	0·0631	0·252	0·0315
40°	0·0875	0·328	0·0352
50°	0·1100	0·407	0·0389
60°	0·1262	0·480	0·0440
70°	0·1430	0·580	0·0480
80°	0·1798	0·680	0·0527
85°	0·2190	0·755	0·0541

Strong acids and potassium hydrogen tartrate dissolve calcium tartrate, and hence it is frequently present in purified tartars. It is precipitated from these solutions by ammonium hydroxide immediately or after some time. It is soluble in ammonium chloride and cold alkali, being reprecipitated from the latter on boiling. Alkali chlorides dissolve it more readily than does water (Cantoni and Jolkowsky, Bull. Soc. chim. 1907, [iv.] 1, 1181). A hot neutral solution of copper chloride converts it on digestion into insoluble copper tartrate, this reaction distinguishing it from calcium citrate; this test, however, will not detect calcium tartrate in the presence of much calcium citrate. Unlike calcium racemate and calcium oxalate, calcium tartrate is soluble in acetic acid.

Crude calcium tartrate is liable to undergo decomposition either by an anaerobic ferment, which yields formic, acetic, butyric, and higher fatty acids, but not propionic acid; or by an aerobic ferment yielding calcium carbonate as the ultimate product (Ordonneau, *ibid.* 1911, [iv.] 9, 398; *cf.* Emmerling, Centr. Bakt. Par. 1908, [ii.] 21, 317). *Bacillus Tartaricus*, which is capable of anaerobic and aerobic life, but which is more active in the latter state, decomposes calcium tartrate with the formation of acetic and succinic acids, hydrogen and carbon dioxide (Grimbert and Ficquet, J. Pharm. Chim. 1898, [vi.] 7, 97).

Calcium hydrogen tartrate $(C_4H_5O_6)_2Ca$ is formed by dissolving the normal salt in tartaric acid, and is much more soluble than the normal salt, 100 parts of water dissolving 0·71 parts of the acid salt at 15·6°.

Strontium tartrate $C_4H_4O_6Sr,3H_2O$ and *barium tartrate* $C_4H_4O_6Ba$ are more soluble than the calcium salt (p. 411). A tribasic barium tartrate has been prepared by Quartaroli (Staz. sperim. agrar. ital. 1910, 43).

Aluminium tartrate $(C_4H_4O_6)_3Al_2$ is formed by dissolving alumina in tartaric acid and is a gummy non-deliquescent mass soluble in water; the solution is capable of dissolving considerable quantities of alumina without becoming alkaline. A double salt of potassium and aluminium appears to be formed by dissolving alumina in cream of tartar. It forms an amorphous mass not precipitated by alkalis, and probably constitutes the active ingredient of the mixture of alum and cream of tartar used in the mordant bath for dyeing wool.

Ferrous tartrate $C_4H_4O_6Fe$ is obtained as a white, almost insoluble, crystalline powder by boiling iron filings with tartaric acid. 100 parts of water at 15·6° dissolve 0·877 parts of the salt (Dulk, Annalen, 1832, 2, 62).

Ferric tartrate $(C_4H_4O_6)_3Fe_2$ is obtained by dissolving the precipitated hydroxide in tartaric acid. The solution deposits a basic salt on warming, but is not precipitated by addition of alkalis on account of the production of a double salt (*cf.* Rosenthaler and Siebeck, Arch. Pharm. 1908, 246, 51).

Nickel tartrate and *cobalt tartrate* and double salts with potassium tartrate are described by Tower (J. Amer. Chem. Soc. 1900, 22, 501; *cf.* Werther, J. pr. Chem. 1844, [i.] 32, 400; Fabian, Annalen, 1857, 103, 248).

Zinc tartrate $C_4H_4O_6Zn.2H_2O$ is prepared by the action of tartaric acid on zinc acetate (Schiff, Annalen, 125, 146) or by boiling tartaric acid with zinc (Frisch, J. 1866, 401). The solubility of zinc, copper, and lead tartrates is given in the following table (Cantoni and Zachovers, Bull. Soc. chim. 1905, [iii.] 33, 754; *cf.* Partheil and Hübner, Arch. Pharm. 1903, 241, 413):—

Temp.	Grms. of salt in 100 c.c. water		
	$C_4H_4O_6Zn,2H_2O$	$C_4H_4O_6Cu,3H_2O$	$C_4H_4O_6Pb$
15°	0·019	0·0197	0·0
20°	0·022	0·0420	—
25°	0·036	0·0690	—
30°	0·041	0·0890	—
40°	0·060	0·1420	0·0015
50°	0·087	0·1920	0·00225
55°	0·116	0·2124	0·00295
60°	0·104	0·1970	0·00305
70°	0·088	0·1640	0·0032
80°	0·059	0·1440	0·0038
85°	0·041	0·1370	0·0054

Copper tartrate $C_4H_4O_6Cu,3H_2O$ is obtained as a greenish-blue crystalline powder on addition of copper sulphate to a soluble tartrate. It dissolves in alkalis and ammonia with formation of double tartrates and the deep blue solution is reduced, with precipitation of cuprous oxide, by heating with glucose and many other organic compounds (*v.* FEHLING'S SOLUTION). For solubility *v. supra.*

Lead tartrate $C_4H_4O_6Pb$ is prepared by the addition of tartaric acid to a soluble lead salt when it forms a white crystalline powder (sp.gr. 3·871) almost insoluble in water (*v. supra*), but readily dissolved by alkalis. It is also obtained by boiling lead acetate with tartaric acid (Heintz, J. 1860, 261; Frisch, *ibid.* 1866, 400). By boiling an ammoniacal solution of the normal tartrate, the insoluble basic tartrate $C_4H_2O_6Pb_2$ is obtained (Erdmann, Annalen, 1837, 21, 19).

Silver tartrate v. SILVER.

Antimony tartrate v. ANTIMONY.

Bismuth tartrate. According to Baudran on boiling bismuth hydroxide with tartaric acid, bismuthotartaric acid $C_4H_5O_6(BiO),H_2O$ is obtained, and by replacement of a hydrogen atom by potassium, an emetic is produced. Similar salts may be obtained containing manganese, iron, or chromium in place of bismuth (Ann. Chim. Phys. 1900, [vii.] 14, 506). Telle states that the compound forms small needles and has the constitution $C_8H_8O_{12}Bi,3H_2O$ and that it may also be obtained by adding tartaric acid to the hydrated lactate of bismuth (Arch. Pharm. 1908, 246, 484). It is almost insoluble in water. Fischer and Grützner state that by boiling freshly precipitated bismuth hydroxide with tartaric acid the compound $C_4H_4O_6,2Bi(OH)_2$ is formed as a white, amorphous, electrical precipitate (*ibid.* 1894, 232, 460).

Esters. The normal esters of tartaric acid may be prepared (i.) by saturating a solution of tartaric acid in the alcohol required with hydrogen chloride; (ii.) by heating an alkyl hydrogen tartrate in a sealed tube with the corresponding alcohol; (iii.) by the action of an alkyl iodide on silver tartrate. If the last method be used a small quantity of the alkyl dialkyloxy compound is also formed, and this has a high rotation (Rodger and Brame, Chem. Soc. Trans. 1898, 301; Purdie and Lander, *ibid.* 1899, 156).

Methyl tartrate $C_4H_4O_6(CH_3)_2$ is a crystalline solid, m.p. 48°; b.p. 280°; 163°/23 m.m.; sp.gr. 1·3403 at 15° (in liquid state); $a_D + 2·74°$. It remains liquid below its boiling-point for a considerable time (Anschütz and Pictet, Ber. 1880, 13, 1176; Anschütz, *ibid.* 1885, 18, 1399; Frankland and Wharton, Chem. Soc. Trans. 1896, 1310).

Ethyl tartrate $C_4H_4O_6(C_2H_5)_2$ is a colourless liquid, b.p. 280°; 162°/19 mm.; sp.gr. 1·2097 at 14° (Anschütz and Pictet, *l.c.*; *cf.* Frankland and McCrae, *ibid.* 1898, 73, 310); $a_D^{20°} + 9·30°$ (Frankland and Wharton, *l.c.*). The influence of solvents, temperature, &c., on the rotation of ethyl tartrate has received considerable attention, *v.* POLARIMETRY and following references: Frankland, *ibid.* 1899, 349; Patterson, *ibid.* 1901, 167, 477; 1903, 765; 1905, 313; 1908, 1836; Patterson and McMillan, *ibid.* 1907, 504; Patterson and McDonald, *ibid.* 1908, 936; 1909, 321; Patterson and Montgomerie, *ibid.* 1130; Patterson and Anderson, *ibid.* 1912, 1833; Purdie and Barbour, *ibid.* 1901, 971; Grossmann, Zeitsch. physikal. Chem. 1910, 73, 148. By passing hydrogen chloride into ethyl alcohol and then adding methyl tartrate and finally boiling under a reflux apparatus, ethyl tartrate is produced. The reverse reaction may also be accomplished (Patterson and Dickinson, Chem. Soc. Trans. 1901, 280). Alkyl metallic salts of the type $C_4H_4O_6RM$ have been prepared.

Methyl hydrogen tartrate $C_4H_5O_6·CH_3$ is prepared by boiling methyl alcohol (1 mol.) with tartaric acid (1 mol.). It forms rhombic crystals containing $1H_2O$ (Tannhaüser, Zeitsch. Kryst. Min. 1908, 45, 183; Marckwald and Karczag, Ber. 1909, 42, 1518).

Ethyl hydrogen tartrate $C_4H_5O_6·C_2H_5$ is prepared by dissolving tartaric acid in an equal quantity of absolute alcohol in a retort at 60°–70°, diluting with water and crystallising the product. It forms rhombic prisms, m.p. 90° (Guerin, *l.c.*).

Detection. Tartaric acid and tartrates char when heated, giving a smell resembling that of burnt sugar. Tartrates leave a residue consisting of the oxide or carbonate of the metal. Tartaric acid and tartrates char very readily when heated with strong sulphuric acid. To distinguish from citric acid or citrates, the substance is heated with pure concentrated sulphuric acid at 100° for 40 minutes. In the presence of tartaric acid the liquid becomes blackened, even as little as 1 p.c. in the substance treated giving a brown shade, whereas citric acid only imparts a yellow colour.

With neutral solutions of tartrates calcium chloride gives a white crystalline precipitate of calcium tartrate. This precipitation only takes place after some time from dilute solutions and may be accelerated by scratching the sides of the containing vessel with a glass rod. If calcium acetate be used as the reagent, solutions containing 0·1 p.c. of tartaric acid give a precipitate, but by adding a few drops of *l*-tartaric acid or its ammonium salt a precipitate is formed in solutions containing only 0·0001 p.c. of tartaric acid, since calcium racemate is less soluble than calcium tartrate (Brönsted, Zeitsch. anal. Chem. 1903, 42, 15). For microscopical detection of calcium tartrate, *v.* Sullivan and Crampton, Amer. Chem. J. 1906, 36, 419.

Potassium acetate and acetic acid, when added to solutions of tartrates or of tartaric acid, yield a colourless precipitate of potassium hydrogen tartrate (de la Source, Compt. rend. 1895, 121, 774).

Silver nitrate gives with neutral solutions of tartrates a white precipitate of silver tartrate. A silver mirror is obtained by heating an ammoniacal solution of silver tartrate. The procedure is as follows: The silver tartrate is treated with ammonium hydroxide in a clean test tube, until it is nearly all dissolved. A crystal of silver nitrate is placed in the bottom of the test tube, which is then transferred to a beaker of boiling water. In a short time a silver mirror is produced on the sides of the tube.

If a few centigrams of resorcinol are heated with about 2 c.c. of concentrated sulphuric acid until vapours are evolved, and a small quantity of a tartrate is added, a bright-red coloration is produced. Or 2 grams of resorcinol may be dissolved in dilute sulphuric acid (0·5 c.c. to 100 c.c. of water) and this used as the reagent. Two or 3 drops are added to 2 c.c. of concentrated sulphuric acid, and to this a very small quantity of the substance (liquid or solid). The solution is then heated at 115°–140° (Denigès, J. Pharm. Chim. 1895, [vi.] 1, 586; Bull. Soc. chim. 1909, [iv.] 5, 19; Mohler, *ibid.* 1890, [ii.] 4, 728). If pyrogallol is substituted for resorcinol, a violet-blue coloration is produced, whilst with β-naphthol the colour is blue in the cold, changing to an intense green on heating, and on dilution with 15–20 volumes of water, a permanent reddish-yellow colour is obtained (Piñerua, Compt. rend. 1897, 124, 291).

On adding a few drops of ferrous sulphate solution followed by a small quantity of hydrogen peroxide to a solution of a tartrate, a yellow coloration is produced, changing to violet on the addition of alkali hydroxide. The colour is discharged by acids and restored by alkalis (Fenton, Chem. Soc. Proc. 1893, 113).

If a few c.c. of cobalt nitrate solution be added to a solution of an alkali tartrate, a red colour is obtained which is discharged by alkali hydroxide. On boiling a blue coloration is produced, which disappears on cooling and reappears on heating (Tocher, Pharm. J. 1906, 77, 87).

Another test consists in boiling the neutral solution with minium. After filtering, a few drops of a 2 p.c. solution of potassium thiocyanate are added. On standing the liquid darkens owing to a precipitation of lead sulphide In testing wines a brownish-violet precipitate is obtained (Ganassini, Boll. Chim. Farm. 1903, 42, 513; Tagliavini, *ibid.* 1907, 46, 493).

Estimation. Since all tartrates leave an oxide or carbonate on gentle ignition, they may be estimated by dissolving the residue in standard acid and determining the amount of acid thus neutralised with standard alkali.

For the estimation of free tartaric acid, alone or in the presence of citric acid, Allen recommends the following process (Chem. News, 1875, 31, 277): 2 grams of the sample are dissolved in 20 c.c. of proof spirit, and the filtered solution is diluted to 45 c.c. with proof spirit, treated with 5 c.c. of a cold saturated solution of potassium acetate, and stirred for 10 minutes. The crystalline precipitate of potassium hydrogen tartrate is filtered off, washed with proof spirit, and, to remove any citrate carried down by the tartrate, is rinsed from the filter by a cold saturated solution of potassium hydrogen tartrate and digested therewith for a few hours. It is then again filtered, washed with proof spirit, rinsed with hot water into a weighed dish, and weighed after evaporating off the water at 100°. The precipitate may be dissolved and titrated with decinormal alkali and phenolphthalein instead of being weighed.

Tartaric acid liquors. These are the liquids obtained by the decomposition of calcium tartrate by sulphuric acid and are of a very complex nature. They contain free tartaric acid; other organic acids; sulphuric acid, and calcium, potassium, aluminium, and iron sulphates; phosphates and bodies of an indefinite nature. The analyst is usually required to estimate the tartaric acid, free sulphuric acid, and in some cases the total organic acids.

For the estimation of tartaric acid potassium acetate is the best reagent for pure liquors, but cannot be used in the presence of iron or aluminium. In the latter case potassium citrate is used. A quantity of liquor containing 2–4 grams of tartaric acid (about 30–40 c.c.) is treated drop by drop with constant stirring with a saturated solution of potassium citrate until, the sulphuric acid having been converted into potassium sulphate, the citrate commences to react with the tartaric acid, which is precipitated as potassium hydrogen tartrate in streaks on the sides of the vessel. If much sulphuric acid is present a fine precipitate of potassium sulphate precedes the appearance of the bitartrate. When the streaks begin to appear, a cubic centimetre of the citrate solution is added for every gram of tartaric acid supposed to be present, in all cases avoiding a great excess of the reagent. If a gelatinous precipitate should appear, the estimation is repeated with the previous addition of some citric acid. After stirring continuously for 10 minutes at a temperature not exceeding 15°, the precipitate is washed two or three times with 25 c.c. of a 5 p.c. solution of potassium chloride, saturated with potassium hydrogen tartrate. The precipitate is then collected on a small filter and washed with the same solution until the acidity of the filtrate is only slightly greater than that of the washing solution. The filter and precipitate are then transferred to a beaker and the amount of tartaric acid estimated by titration against standard alkali, phenolphthalein or litmus being used as an indicator. Sometimes a potassium hydrogen citrate is carried down with the tartrate and is difficult to separate. The best method is to dissolve the precipitate in 50 c.c. of hot water, add 5 grms. of potassium chloride, and cool the liquid quickly to 15° with continuous stirring for 10 minutes. This purified precipitate is then washed with the washing liquid and treated as above, but a correction of 0·5 p.c. must be added to the percentage of tartaric acid so found to allow for unavoidable losses in the purification process. From very old liquors containing much sulphuric acid potassium alum may be precipitated owing to its sparing solubility in solutions of potassium sulphate. To prevent this phosphoric acid should be added before the citrate solution, and the liquid filtered immediately after stirring. For further details *v.* Allen's Commercial Organic Analysis, 1911, i. 541.

To estimate the free sulphuric acid, 20 c.c. of the liquid are made up to 200 c.c. with alcohol and allowed to remain overnight. The liquid is then filtered through a dry filter, and the alcohol evaporated from 100 c.c. of the filtrate. The sulphuric acid is then estimated as barium sulphate in the usual manner (Allen, *ibid.* 549).

To estimate the total organic acids, a known volume of the liquor is exactly neutralised with standard alkali and the liquid evaporated to dryness. The residue is ignited at a very low temperature until the carbon is nearly all burnt away. The ash is heated with a known volume of standard sulphuric acid, the solution decanted and the insoluble residue heated with more standard acid, concentrating the solution, if necessary, to dissolve the phosphates. To the mixed cold concentrated solutions, sufficient sodium potassium tartrate is added to keep any aluminium in solution and the solution titrated with standard alkali using litmus as an indicator. Each c.c. of normal sulphuric acid neutralised by the ash is equivalent to 0·075 grm. of organic acid, expressed in terms of tartaric acid (Warington. J. Chem. Soc. 1876, 28, 982).

Lees, argols, and *tartars.* About 8 grms. of the lees or argol (or 3 grms. of tartar) are heated on the water-bath with a little water for 5 minutes. Two grams of potassium oxalate are added and the mixture heated for a further 15 minutes. While hot the solution is nearly neutralised with a 3·5 p.c. solution of potassium hydroxide, the quantity of alkali being about 0·5 p.c. below that required for complete neutralisation, as determined by a preliminary experiment (*v. infra*). The solution is then heated on the water-bath for 30 minutes and the precipitate filtered off with the aid of a filter pump. The precipitate is washed ten times with water, using 3 c.c. each time, and the filtrate should have a volume of 50 c.c.; to this solution are added 5 grms. of potassium chloride and 2·5 grms. of citric acid, and after stirring continuously for 10 minutes, the solution is allowed to stand for 30 minutes. The precipitated potassium hydrogen tartrate is filtered off and washed with a 10 p.c. solution of potassium chloride saturated with potassium hydrogen tartrate, the acidity of which has been previously determined with N/10 alkali. When the acidity of the washings is the same as that of the washing solution the precipitate is dissolved in hot water and titrated with N/10 potassium hydroxide. The preliminary determination of the acidity of the sample is carried out as follows: Exactly 3 grms. of the sample are extracted with boiling water, the liquid decanted off and the operation repeated. The residue is transferred to a filter paper and washed until the washings are no longer acid. The solution is then titrated with 3·5 p.c. potassium hydroxide solution, using neutral litmus paper as an indicator (Allen, *ibid.* 546; Warington, *l.c.*; Grosjean, Chem. Soc. Trans. 1879, 34).

Total tartaric acid. Many methods have been proposed for the analysis of tartar and at the Seventh International Congress of Applied Chemistry, the method of Goldenberg, Geromont

& Co. was adopted as being most suitable (Zeitsch. anal. Chem. 1908, 47, 57). A weighed amount of the sample (6 grms. if the tartaric acid yield is likely to be above 45 p.c.; 12 grms. if below that percentage) is digested with 18 c.c. of hydrochloric acid of sp.gr. 1·1 for 10 minutes. The whole mass is then washed into a 200 c.c. graduated flask, made up to the mark with distilled water, shaken well and filtered through a dry filter into a dry flask. 100 c.c. of the filtered liquid are then poured into a 300 c.c. beaker, containing 10 c.c. of potassium carbonate solution (66 grms. of pure carbonate in 100 c.c.). The solution is brought to boiling and kept at that point for 20 minutes until the calcium carbonate has separated in a crystalline form. The liquid and precipitate are rinsed into a 200 c.c. flask, made up to the mark and filtered through a dry filter. 100 c.c. of the filtrate are transferred to a porcelain basin and evaporated to 15 c.c. While the liquid is still hot, 3·5 c.c. of glacial acetic acid are added gradually with constant stirring, which is maintained for 5 minutes after the acid has been added. After standing for 10 minutes, 10 c.c. of 95 p.c. alcohol are added and the liquid stirred for another 5 minutes. The liquid is allowed to stand for a further 10 minutes and then filtered with the aid of a pump and washed with alcohol until the washings are no longer acid (*v. infra*). The filter and precipitate are transferred by means of 200 c.c. of hot water into a porcelain basin, the liquid brought to boiling and titrated with N/5 alkali, using neutral litmus paper as the indicator. The alkali must have been standardised against pure potassium hydrogen tartrate, using the same paper as indicator. A correction has to be made since the volume of undissolved matter has not been allowed for in making the solution up to the various volumes. It was agreed that for samples containing less than 45 p.c. of acid, 0·8 should be deducted.; for those containing from 45 p.c. to 60 p.c., 0·3; from 60 p.c. to 70 p.c., 0·2; and for those containing over 70 p.c. no deduction should be made. To control the washings 30 c.c. of the alcohol is titrated with standard alkali, using phenolphthalein as indicator. The washing is continued until 30 c.c. of the filtrate require the same amount of standard alkali to give the colour that was produced in the test with the original 30 c.c.

This method has been criticised by Heczko (Zeitsch. anal. Chem. 1911, 50, 12), Tobler and Caramelli (J. Soc. Chem. Ind. 1911, 207), Ordonneau (Bull. Soc. chim. 1910, [iv.] 7, 1034) and Beys (Compt. rend. 1910, 150, 1250; Bull. Soc. chim. 1910, [iv.] 7, 697). According to Heczko the results obtained are influenced by the amount of calcium salts present, as they are not completely precipitated by potassium carbonate in the presence of tartrates. Also the insolubility of potassium hydrogen tartrate depends on the temperature and concentration of the solution from which it is precipitated. Tobler and Caramelli state that the error introduced by making the solution up to 200 c.c. after treatment with potassium carbonate increases with the amount of precipitated calcium carbonate, and the suggested corrections do not adequately allow for it. Ordonneau has made a series of determinations by the Goldenberg method, using for the purpose of analysis pure potassium hydrogen tartrate and calcium tartrate to which known quantities of the impurities which occur in tartars were added. He concludes that the error when litmus is used as indicator is double that obtained with phenolphthalein and that the best results are obtained with the latter indicator at 50° after boiling and cooling to that temperature. His results are tabulated below:—

Impurities added to potassium hydrogen tartrate	Total tartaric acid	Percentage of impurity	Loss of tartaric acid		Loss of tartaric acid per gram of impurity.	
			Litmus	Phenolphthalein	Litmus	Phenolphthalein
Calcium phosphate (tribasic) . .	75·80	5	2·35	1·60	0·47	0·32
Ferrous phosphate	75·80	5	6·15	3·68	1·22	0·73
Ferric phosphate	75·80	5	7·95	3·98	1·59	0·79
Aluminium phosphate	75·80	5	4·65	2·20	0·93	0·44
Alumina, pure anhydrous . . .	75·80	5	19·35	8·80	3·87	1·76
Ferric chloride, dry (≡ 4·92 grms. Fe_2O_3)	71·81	10	13·38	7·21	2·71	1·46
Calcium tartrate	78·69	5	1·77	0·99	—	—
Calcium tartrate	77·57	10	1·85	1·04	—	—
Calcium tartrate (alone) . . .	57·69	—	2·08	2·00	—	—

Lead in tartaric acid. The following method is due to W. A. Davis (Allen's Commercial Organic Analysis, 1911, i. 550, 569; *cf.* Wilkie, J. Soc. Chem. Ind. 1909, 28, 637). The reagent is freshly prepared colourless ammonium sulphide, obtained by diluting 2 c.c. of 0·880 ammonia to 10 c.c. and saturating with well-washed hydrogen sulphide. Standard lead solutions are made by dissolving 5 grams of pure lead in nitric acid, evaporating to remove all but the last traces of nitric acid and diluting to 1000 c.c. For use portions of it are taken, diluted 100 times and treated in the usual manner for colour comparisons.

Ten grams of tartaric acid are dissolved in 25 c.c. of hot water, cooled, and to the solution are added 2 c.c. of N/10 sodium thiosulphate solution. The solution is heated nearly to boiling, cooled, and 1 c.c. of a 10 p.c. solution of potassium cyanide is added. Then ammonia (0·880) is added until the liquid has a faint smell of the reagent. The liquid is boiled until it is colourless, poured into a tall cylinder, made up to 100 c.c. and treated with 2 drops of the freshly prepared reagent. The tint obtained is compared with tints produced by solutions made from pure lead-free tartaric acid to which known amounts of the lead nitrate solution have been added, so as to give comparisons of the order of 5 parts per 1,000,000, 10 parts per 1,000,000, &c. If it is desired to test cream of tartar, 10 grams should be dissolved in hydrochloric acid and after the addition of sodium thiosulphate, the above method can be used.

Wines. For estimating tartaric acid in wines the method of Kling may be used (Compt. rend. 1910, 150, 616; Bull. Soc. chim. 1912, [iv.] 11, 886). 25 c.c. of the solution, diluted or concentrated so as to contain 3–4 grms. of tartaric acid per litre, are added to 100 c.c. of water. To the solution are added 25 c.c. of a solution of *l*-potassium sodium tartrate (16 grms. per litre) and 20 c.c. of a solution of calcium acetate (30 grms. per litre). The precipitated calcium racemate is filtered off, washed, and dissolved in 20 c.c. of hydrochloric acid (40 grms. per litre). The solution is diluted to 150 c.c. and 40 c.c. of a solution of sodium acetate (10 p.c.) and calcium acetate (1 p.c.) is added and the liquid heated to boiling. After cooling the racemate is collected, washed, dissolved in boiling dilute sulphuric acid and titrated at the boiling-point with potassium permanganate solution (16 grms. per litre), which has been standardised against potassium hydrogen tartrate. In the presence of considerable amounts of iron or aluminium salts, &c., the initial precipitation must be performed in the presence of ammonium citrate (Kling and Florentin, Ann. Falsif. 1912, 5, 518). For other methods of estimation in wines, *v.* Gowing-Scopes, Analyst, 1908, 33, 315; von Florentz, Chem. Zeit. 1907, 31, 1118.

l-Tartaric Acid.

This acid, which has also been called *anti-tartaric acid*, was first obtained by Pasteur (Ann. Chim. Phys. 1850, [iii.] 28, 56) by the crystallisation of a solution of sodium ammonium racemate. The product was found to consist of a mixture of hemihedral crystals, some having the hemihedral faces developed to the right and others to the left, the former being dextrorotatory, and the latter lævorotatory. The acid obtained from the former was *d*-tartaric acid, while the latter yielded a lævorotatory acid, *l*-tartaric acid (*cf.* Bichat, Bull. Soc. chim. 1886, [ii.] 46, 54; Jungfleisch, J. 1883, 1084). The best method of preparation is that due to Marckwald (Ber. 1896, 29, 42; *cf.* Kling, Bull. Soc. chim. 1910, [iv.] 7, 774). To a boiling aqueous solution of racemic acid is added gradually half the amount of cinchonine necessary to form the acid salt and sufficient water to give a clear solution. After standing for one day cinchonine *l*-tartrate crystallises out, from which *l*-tartaric acid can be obtained in the usual manner. The yield is two-thirds of that demanded by theory. For asymmetric synthesis by the action of potassium permanganate on *l*-bornyl fumarate, *v.* McKenzie and Wren, Chem. Soc. Trans. 1907, 1215.

Properties. *l*-Tartaric acid forms anhydrous rhombic crystals, m.p. 168°–170° (Bischoff and Walden, Ber. 1889, 22, 1820; Zeitsch. physikal. Chem. 1891, 8, 466). It resembles *d*-tartaric acid in most of its physical properties (*v.* p. 403), but the two acids are oppositely pyroelectric and also solutions of the same concentration rotate the plane of polarised light an equal amount, but in opposite directions. Solutions of *l*-tartaric acid are destroyed by *Schizomycetes.* The salts of *l*-tartaric acid have the same number of molecules of water of crystallisation and the same crystalline form as those of *d*-tartaric acid. They exhibit opposite hemihedry, opposite rotation and are oppositely pyroelectric. They are also somewhat more soluble than the corresponding salts of the *d*-acid (Jungfleisch, Bull. Soc. chim. 1884, [ii.] 41, 223). There are differences between the compounds of the two acids with optically active substances. Thus a partially racemic compound is obtained by the combination of ammonium *d*-tartrate and ammonium *l*-malate, whilst ammonium *l*-tartrate does not undergo this combination (*v.* Racemism). The compounds with optically active bases also are different, thus cinchonine *d*-tartrate crystallises with $4H_2O$, whilst the *l*- salt only has $1H_2O$, but the affinity constants of *d*- and *l*-tartaric acids for optically active bases are the same (Marckwald and Chwolles, Ber. 1898, 31, 783).

Racemic Acid.

This acid, which is also known as r-*tartaric acid* or *paratartaric acid*, was discovered by Kestner in the mother liquors of tartaric acid obtained from the vintage of 1822 (Compt. rend. 1849, 29, 526, 557) and was examined by Gay-Lussac (Schweiger's J. 48, 381), Walchner (*ibid.* 49, 238), Berzelius (Pogg. Annalen, 19, 319), and Biot (Ann. Chim. Phys. [ii.] 69, 22), of whom the last-named pointed out its optical inactivity. Pasteur investigated its properties further and decomposed it into *d*- and *l*-tartaric acids (Compt. rend. 1853, 36, 19; 37, 162). Racemic acid appears to exist to some extent in grape juice, but is produced chiefly during the fermentation. It is produced to a certain extent in the tartaric acid works in the process of purification, and after crystallising cream of tartar, potassium ammonium racemate can be extracted from the mother liquors.

Preparation. Most methods for the production of racemic acid result also in the formation of mesotartaric acid, from which it may be separated by the method given on p. 404. The following are the chief methods for the interconversion of the tartaric acids. When *d*-tartaric acid is heated for 30 hours at 170° with one-seventh to one-tenth of its weight of water, racemic acid is the main product, whilst by heating *d*-tartaric acid (or racemic acid) with 4 c.c. of water for 2 days at 165°, mesotartaric acid is produced (Jungfleisch, Bull. Soc. chim. 1872, [ii.] 18, 203; 1873, [ii.] 19, 101; 1874, [ii.] 21, 146; 1878, [ii] 30, 191; *cf.* Dessaignes, *ibid.* 1863, [i.] 5, 356). According to Meisner, the yield of mesotartaric acid is only 5·5 p.c. by this method, and if 100 grms. of *d*-tartaric acid are heated with 350 grms. of sodium hydroxide, and 700 grms. of water during 8 hours in a copper flask, racemic acid is obtained almost free from mesotartaric acid, only 1·3 p.c. of the latter being produced (Ber.

1897, 30, 1574). Holleman states that by heating *d*-tartaric acid for 8 hours with boiling alkali, 24 p.c. of mesotartaric acid is produced, the maximum yield of 31 p.c. being obtained after only 2 hours' heating (Rec. trav. chim. 1898, 17, 66; *cf.* Bosekin, *ibid.* 224). Holleman also heated 6 grms. of *d*-, *r*-, and *i*-tartaric acids wth 4 c.c. of N-hydrochloric acid in sealed tubes and obtained the following results. *d*-Tartaric acid below 140° yielded *i*-tartaric acid almost entirely, but after 42 hours at 155°, 6·7 p.c. of *r*-tartaric acid and 18 p.c of *i*-tartaric acid were obtained. *r*-Tartaric acid, after 100 hours at 140°, yielded 19 p.c. of *i*-tartaric acid, and the latter under similar conditions gave 10 p.c. of the *r*-tartaric acid. Finally when *d*- and *l*-tartaric acids are mixed in equal quantities in solution, racemic acid is the sole product.

By heating dibromosuccinic acid or dibromo*iso*succinic acid with 200 parts of water, a mixture of mesotartaric and racemic acids is obtained, the former yielding chiefly mesotartaric acid and the latter racemic acid (Lossen and Riebensahm, Annalen, 1896, 292, 295; *cf.* Pasteur, Annalen, Suppl. 2, 242). A similar result is obtained by using the silver salt (Perkin and Duppa, Quart. J. Chem. Soc. 1861, 13, 112; Kekulé, Annalen, 1860, 117, 121). By heating an alcoholic solution of glyoxal with a 5 p.c. excess of alcoholic hydrocyanic acid, a mixture of the nitriles of racemic and mesotartaric acids is produced (Pollak, Monatsh. 1894, 15, 469; Strecker, Zeitsch. Chem. 1868, 216; Schöyen, Annalen, 1864, 132, 168; Staedel, Ber. 1878, 11, 752). When phenol is oxidised with potassium permanganate in alkaline solution a mixture of *r*- and *i*-tartaric acids is obtained (Doebner, Ber. 1891, 24, 1755).

Racemic acid may be obtained by reducing glyoxylic acid with zinc and acetic acid, glycollic acid also being produced (Genvresse, Compt. rend. 1892, 114, 555); by oxidising fumaric acid with potassium permanganate (Kekulé and Anschütz, Ber. 1880, 13, 2150; Annalen, 1884, 226, 191; *cf.* Tanatar, Ber. 1879, 12, 2293); by treating piperic or sorbic acid with dilute potassium permanganate solution (Doebner, *ibid.* 1890, 23, 2374); by the action of nitric acid on fructose, mucic acid, and inulin, the first-named also yielding mesotartaric acid (Kiliani, *ibid.* 1881, 14, 2530); and together with *d*-tartaric acid by the action of nitric acid on dulcitol, mannitol, milk sugar, cane sugar, and saccharic acid (Carlet, J. 1860, 249; 1861, 367; Hornemann, J. pr. Chem. 1861, [i.] 89, 283).

Properties. Racemic acid crystallises in large plates belonging to the triclinic system and which contain 1 mol. of water of crystallisation. It is less soluble in water or alcohol than tartaric acid, and has m.p. 205°–206°; sp.gr. 1·697 (Walden, Ber. 1896, 29, 1701). The reactions which it undergoes are the same as those of tartaric acid.

The racemates resemble the tartrates in most respects, but differ in their solubility and in the number of molecules of water of crystallisation which they contain. Thus *potassium racemate* crystallises in the rhombic system with $1H_2O$, or in the monoclinic with $2H_2O$ (van 't Hoff and Müller, Ber. 1899, 32, 857), whilst the *rubidium salt* crystallises in the monoclinic system with $2H_2O$ at low temperatures; at higher temperatures the solution deposits crystals of rubidium *d*- and *l*-tartrates (Traube, Sitzungsber. Berl. Akad. 1895, 10, 195; Wyrouboff, Chem. Zentr. 1901, ii. 764; *cf.* van't Hoff and Müller, Ber. 1898, 31, 2206). *Calcium racemate* crystallises in fine needles containing $4H_2O$, and is obtained by adding calcium sulphate to a soluble racemate or racemic acid. It is even less soluble than calcium tartrate, and use is made of this fact in Kling's method for the estimation of tartaric acid (*v.* p. 416). For distinction from calcium tartrate *v.* p. 412. The *barium salt* crystallises with $2\frac{1}{2}H_2O$ and with $5H_2O$ (Lossen and Riebensahm, Annalen, 1896, 292, 313; Mügge, Chem. Zentr. 1899, ii. 245). For resolution of racemates into *d*- and *l*-tratrates, *v.* RACEMISM.

MESOTARTARIC ACID.

Mesotartaric acid, which is also known as i-*tartaric acid*, was first obtained by Pasteur, together with racemic acid, by heating cinchonine *d*- or *l*-tartrate for some time at 170°. Most of the methods of preparation result also in the production of racemic acid, the best being that of Holleman (*v. Racemic acid*). It may also be obtained by treating mesodiaminosuccinic acid with nitrous acid (Farchy and Tafel, Ber. 1893, 26, 1986; *cf.* Lehrfeld, *ibid.* 1881, 14, 1819), or by oxidising sorbin (Dessaignes, Annalen, Suppl. 2, 242), erythritol (Przybtek, J. Russ. Phys. Chem. Soc. 1880, 12, 209) or glycerol (*ibid.* 1881, 13, 330) with dilute nitric acid.

It crystallises in rectangular plates containing 1 mol. of water of crystallisation, and has m.p. 140° and sp.gr. 1·666 (Bischoff and Walden, Ber. 1896, 29, 1702). It is slightly less soluble in water than tartaric acid. Its affinity constant is 0·060. The mesotartrates resemble the tartrates except in their solubility and in the number of molecules of water of crystallisation which they contain. Thus the *calcium salt* contains $3H_2O$ and, like the potassium salt, is more soluble than the corresponding salt of tartaric acid. Marckwald and Karczag (Ber. 1909, 42, 1518) have prepared two optically active methyl hydrogen mesotartrates by boiling mesotartaric acid with methyl alcohol and resolving the resulting racemic ester with strychnine.

TARTRAZINE *v.* PYRAZOLONE COLOURING MATTERS.

TARTRONIC ACID, *hydroxymalonic acid* $HO{\cdot}CH(CO_2H)_2$, discovered by Dessaignes in 1853 as a decomposition product of an aqueous solution of dinitrotartaric acid and hence named *tartronic acid* (Annalen, 1852, 82, 363; 1854, 89, 339; compare Demole, Ber. 1877, 10, 1788); is also obtained by reducing mesoxalic acid with sodium amalgam (Deichsel, Zeitsch. Chem. 1865, 69); by the action of baryta water or of silver oxide on monobromomalonic acid (Pinner, Ber. 1875, 8, 963; Petrieff, *ibid.* 1878, 11, 414); by hydrolysing ethyl monochloromalonate with potassium hydroxide and decomposing the calcium salt with oxalic acid (Conrad and Bischoff, *ibid.* 1880, 13, 595); by the action of baryta water on dibromopyruvic acid (Grimaux, Bull. Soc. chim. 1877, [ii.] 27, 440); or of dilute sodium hydroxide on ethyl trichlorolactate (Pinner, 1885, Ber. 18, 752). Tartronic acid can be obtained by the careful oxidation of glycerol with nitric acid (Sadtler, *ibid.* 1875, 8, 1456) or potassium permanganate (Campani and Bizzarri, Gazz. chim. ital. 1880, 10, 489; compare *ibid.* 1883, 13, 490); and it has been synthesised by treating glyoxylic acid with potassium cyanide and boiling the product with baryta water (Böttinger, Ber. 1881, 14, 729). Tartronic acid is most conveniently prepared by heating an aqueous solution of dihydroxytartaric acid until carbon dioxide ceases to be evolved and finally evaporating the solution (Fenton, Chem. Soc. Trans. 1898, 73, 73; compare Grüber, Ber. 1879, 12, 514).

Tartronic acid crystallises from water in large, hard, anhydrous prisms; it sublimes when carefully heated at 110°–120° (Conrad and Bischoff, *l.c.*); melts at 158°–159° (Fenton, *l.c.*; Skinner, Chem. Soc. Trans. 1898, 73, 489); at 155° (Grüber, *l.c.*; Massol, Compt. rend. 1892, 114, 422); at 145°–160° (Grimaux, *l.c.*); melts and decomposes at 185°–187° (Conrad and Bischoff, *l.c.*); at 178°–180° (Campani and Bizzarri, Gazz. chim. ital. 1882, 12, 1); at 184° (Pinner, *l.c.*); at 183° (Böttinger, *l.c.*). It has electrical conductivity $\mu_D=357$ (Ostwald, Zeitsch. Physikal. Chem. 3, 369), affinity constant $K=0{\cdot}107$ (Skinner, *l.c.*); for heats of neutralisation compare Gal and Werner (Compt. rend. 1886, 103, 871, and Massol (*l.c.*). It is readily oxidised by hydrogen peroxide in the presence of ferrous salts into mesoxalic acid (Fenton, Chem. Soc. Trans. 1900, 77; 71).

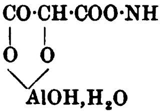
Salts. Tartronic acid forms both normal and acid salts, which, with the exception of the salts of the alkali metals, are insoluble or only sparingly soluble in water (Pinner, Ber. 1885, 18, 752). The following salts are described:—*Ammonium* $C_3H_2O_5(NH_4)_2$ and $C_3H_3O_5(NH_4)$ (Dessaignes, *l.c.*); *sodium* $C_3H_2O_5Na_2$ is deliquescent and becomes anhydrous at 110°, the *acid* salt is unstable; *potassium* $C_3H_2O_5K_2$ and

$$C_3H_3O_5K,\tfrac{1}{2}H_2O$$

(Conrad and Bischoff, *l.c.*; Massol, *l.c.*); *barium* $C_3H_2O_5Ba,2H_2O$; *calcium* $C_3H_2O_5Ca,2\tfrac{1}{2}H_2O$ (Pinner, *l.c.*); *zinc* and *mercury* salts are white precipitates, *cobalt* salt is a red flocculent precipitate; the *copper* salt bluish-green crystals (Conrad and Bischoff, *l.c.*); *lead* salts $C_3H_2O_5Pb$ and $(C_3HO_5)_2Pb_3,2H_2O)$; *cadmium* salt $C_3H_2O_5Cd$ (Grüber, *l.c.*); *silver* salt $C_3H_2O_5Ag_2$ is crystalline (Conrad and Bischoff, *l.c.*); *manganese* salt

$$[CO_2H{\cdot}CH(OH){\cdot}COO]_2Mn$$

crystallises in the triclinic system (Campani and Bizzarri, *l.c.*); the aluminium in the complex *aluminium* compound



$$\begin{array}{c} CO{\cdot}CH{\cdot}COO{\cdot}NH_4 \\ |\quad\;\; | \\ O\quad O \\ \diagdown\diagup \\ AlOH,H_2O \end{array}$$

is not precipitated by ammonia (Hamus and Quadrat, Zeitsch. anorg. Chem. 1909, 63, 306).

Derivatives. The *ethyl ester* $HO{\cdot}CH(COOEt)_2$ has m.p. 2°, b.p. 120·5°–121°/15 mm. (Filippo, Rec. trav. chim. 1910, [ii.] 14, 113; Freund, Ber. 1884, 17, 780; Pinner, *l.c.*); it forms an *acetate* $CH(OAc)(CO_2Et)_2$, b.p. 235°–245° under atmospheric pressure, or 158°–163°/60 mm.; of which the *ethyl* derivative $CEt(OAc)(CO_2Et)_2$ has b.p. 151°–153°/30 mm. (Conrad and Brückner, Ber. 1891, 24, 2997); the *phenyl ether*

$$CH(OPh)(CO_2Et)_2$$

has b.p. 230°–240°/60 mm., and yields the crystalline *acid* $CH(OPh)(COOH)_2$ on hydrolysis. The *methyl ester* $HO{\cdot}CH(CO_2Me)_2$ has m.p. 44·5°–45°, b.p. 122°/19 mm. (Filippo, *l.c.*); the *chloro* derivative $HO{\cdot}CCl(CO_2Me)_2$ has m.p. 42°, is unstable and converted into methyl dihydroxymalonate on exposure to moist air; the *bromo* derivative $HO{\cdot}CBr(CO_2Me)_2$, m.p. 30° (decomp.) dissociates at 40° into hydrogen bromide and methyl mesoxalate; the *anilino* derivative $PhNH{\cdot}C(OH)(CO_2Me)_2$ has m.p. 102° and yields methyl phenyliminomalonate $NPh:C(CO_2Me)_2$ by the action of phosphoric oxide (Curtiss and Spencer, J. Amer. Chem. Soc. 1909, 31, 1053).

Tartronamic acid $CO_2H{\cdot}CH(OH)CONH_2$ prepared by boiling freshly prepared sodium dialurate with water, forms large needles or prismatic crystals, m.p. 160° (decomp.), and yields crystalline *barium* $(C_3H_4O_4N)_2Ba,H_2O$, *lead* $(C_3H_4O_4N)_2Pb,\tfrac{1}{2}H_2O$; *potassium*

$$C_3H_4O_4NK,H_2O$$

and *silver* $C_3H_4O_4NAg$ salts (Menschutkin, Annalen, 1876, 182, 82).

Tartronamide $HO{\cdot}CH(CONH_2)_2$ has m.p. 195°–196° (Pinner, *l.c.*), 198° (Freund, *l.c.*) and gives the biuret reaction (Schiff, Ber. 1896, 29, 298, 1354). *Tartrono-dimethylamide*

$$HO{\cdot}CH(CONHMe)_2$$

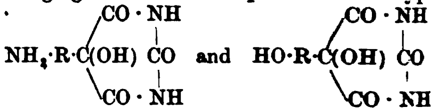
has m.p. 153°–154° (Filippo, *l.c.*).

Alkyl substituted tartronic acids. Methyltartronic acid $HO{\cdot}CMe(CO_2H)_2$ has m.p. 175° (Schmöger, J. pr. Chem. [ii.] 14, 77; 19, 168; 24, 38; Böttinger, Ber. 1881, 14, 87, 148; 1884, 17, 114); *ethyltartronic acid* $HO{\cdot}CEt(CO_2H)_2$ has m.p. 98° (Guthzeit, Annalen, 1881, 209, 232); iso*butyltartronic acid* $HO{\cdot}C(C_4H_9)(CO_2H)_2$ has m.p. 110°–114° (Conrad and Bischoff, Annalen, 1881, 209, 218), *benzyltartronic acid*

$$CH_2Ph{\cdot}C(OH)(CO_2H)_2$$

has m.p. 143°; all these acids decompose at their melting-point, yielding the corresponding member of the acetic acid series.

Aryl substituted tartronic acids. Alloxan condenses with aromatic amines, phenols or polyhydric phenols in the presence of condensing agents to form compounds of the types



$$NH_2{\cdot}R{\cdot}C(OH)\begin{cases}CO{\cdot}NH \\ \qquad\;\; CO \\ CO{\cdot}NH\end{cases} \text{ and } HO{\cdot}R{\cdot}C(OH)\begin{cases}CO{\cdot}NH \\ \qquad\;\; CO \\ CO{\cdot}NH\end{cases}$$

and these are readily hydrolysed by alkali to give the alkali salt of the corresponding substituted tartronic acid

$$NH_2{\cdot}R{\cdot}C(OH)(COOK)_2$$

and $HO{\cdot}R{\cdot}C(OH)(COOK)_2$ from which the acid is usually easily obtained. The following acids obtained by these methods are described in the patent literature (D. R. PP. 107720, 112174, 113722, 114904, 115817):—p-*ethylaminophenyltartronic acid*

$$NHEt{\cdot}C_6H_4{\cdot}C(OH)(CO_2H)_2,$$

m.p. 163° (decomp.); p-*diethylaminophenyltartronic acid* $NEt_2{\cdot}C_6H_4{\cdot}C_3H_3O_5$, m.p. 107°–108° (decomp.); p-*benzylaminophenyltartronic acid* $C_7H_7NH{\cdot}C_6H_4{\cdot}C_3H_3O_5$, m.p. 137° (decomp.); *potassium hydrogen* p-*ethylbenzylaminotartronate* $C_7H_7NEt{\cdot}C_6H_4{\cdot}C_3H_2O_5K$; p-*phenylaminophenyltartronic acid* $NHPh{\cdot}C_6H_4{\cdot}C_3H_3O_5$, m.p. 125°–127° (decomp.); p-*iminodiphenyltartronic acid*

$NH(C_6H_4{\cdot}C_3H_3O_5)_2$ as potassium hydrogen salt only; p-*amino*-m-*tolyltartronic acid*

$$NH_2{\cdot}C_7H_6{\cdot}C_3H_3O_5,$$

m.p. 194°–195° (decomp.); p-*ethylamino*-m-*tolyltartronic acid* $NHEt{\cdot}C_7H_6{\cdot}C_3H_3O_5$; p-*amino*-m-*methoxyphenyltartronic acid*

$$NH_2{\cdot}C_6H_3(OMe)C_3H_3O_5,$$

m.p. 187°–188° (decomp.); p-*methylamino*-m-*methoxyphenyltartronic acid*

$$NHMe{\cdot}C_6H_3(OMe)C_3H_3O_5,$$

m.p. 135° (decomp.); p-*amino*-m-*ethoxyphenyltartronic acid*, m.p. 150° (decomp.); p-*amino*-o-*chlorophenyltartronic acid* $NH_2{\cdot}C_6H_3Cl{\cdot}C_3H_3O_5$, m.p. 198°–199° (decomp.); p-*dimethyl*- and p-*diethyl-amino*-o-*chlorophenyltartronic acids* as potassium hydrogen salts only; p-*ethylenediaminodiphenyltartronic acid* $C_2H_4N_2H_2(C_6H_4{\cdot}C_3H_3O_5)_2$ decomposes at 400°; o-*hydroxyphenyltartronic acid* $HO{\cdot}C_6H_4{\cdot}C_3H_3O_5$, m.p. 118°–120° (decomp.); p-*hydroxy*-m-*methoxy-phenyltartronic acid*; o-*hydroxy*-m-*tolyltartronic acid*; and m-p-*dihydroxyphenyltartronic acid*. M. A. W.

TASMANITE *v.* RESINS.

TAURINE, *a-amino-β-ethanesulphonic acid*

$$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H,$$

in combination with cholic acid forms one of the chief constituents of the bile of oxen and other animals, whence it was obtained by Gmelin in 1826; it was afterwards investigated by Demarçay (Annalen, 1838, 27, 286) and by Dumas and Pelouze (*ibid.* 292), who overlooked the fact that it contained sulphur and gave it the formula $C_2H_7NO_5$. Redtenbacher (*ibid.* 1846, 57, 170), remarking on the strangely inert behaviour towards strong acids of a compound containing so large a proportion of oxygen, reinvestigated the compound, and on fusion with alkali obtained evidence of the presence of sulphur, and gave it the correct formula $C_2H_7NO_3S$. Taurine occurs in the muscles and organs of Bojanus of *Mytilus edulis* (Kelly, Beitr. chem. Physiol. Path. 1904, 5, 377); in the extract of muscle and the hepato-pancreas of various marine gasteropods (Mendel, *ibid.* 582); and in meat extract (Micko, Zeitsch. Nahr. Genussm. 1908, 15, 449; Zeitsch. physiol. Chem. 1908, 56, 180). The source of the taurine in the animal economy is the cystine of the ingested protein, the oxidation occurring in the liver; experiments on dogs serve to show that the administration of cystine leads to an increase in the output of taurine (Von Bergmann, Beitr. chem. Physiol. Path. 1903, 4, 192); and experiments on cats show that if artificial cystinuria is produced there is a consequent fall in the taurine of the bile (Gibson, Proc. Amer. Soc. Biol. Chem. 1908, 16).

Synthesis. Taurine can be synthesised from ethylene by the following series of reactions:—ethylene dibromide is converted by the action of antimony pentachloride into ethylene chlorobromide, which on treatment with potassium thiocyanate yields ethylene chlorothiocyanate; this is converted by oxidation into chloroethylsulphonic acid, the silver salt of which reacts with ammonia at 100°–120°, yielding taurine

$$C_2H_4 \rightarrow C_2H_4Br_2 \rightarrow C_2H_4ClBr \rightarrow C_2H_4Cl(CNS)$$
$$\rightarrow C_2H_4Cl{\cdot}SO_3H \rightarrow C_2H_4(NH_2)SO_3H$$

(James, Chem. Soc. Trans. 1879, 35, 810; compare Kolbe, Annalen, 1862, 122, 33). Taurine can also be readily prepared from cysteic acid (*a*-amino-*β*-sulphopropionic acid) by heating it with water in a sealed tube at 235°–240°

$$SO_3H{\cdot}CH_2{\cdot}CH(NH_2)CO_2H \rightarrow SO_3H{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$$

(Friedmann, Beitr. Chem. Physiol. Path. 1903, 3, 1).

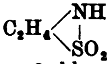
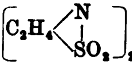
Taurine crystallises in large tetragonal plates, that decompose on heating above 240°; it is soluble in 15·5 parts of water at 12°, or in 25,000 parts of 90 p.c. alcohol at 17° (Stutzer, Zeitsch. anal. Chem. 1892, 31, 503).

When taurine is administered to human subjects or to dogs, it is eliminated partly unchanged and partly in the form of taurocarbamic acid (*v. infra*; Salkowski, Ber. 1873, 6, 744); when fed to fowls a considerable portion reappears unchanged in the excreta, the remainder is oxidised to sulphuric acid (Čech, *ibid.* 1877, 10, 1461).

Salts. Taurine has a neutral reaction, and forms salts with bases, the *silver* $C_2H_6NSO_3Ag$; *lead* $(C_2H_6NSO_3)_2Pb$ and

$$2[(C_2H_6NSO_3)_2Pb],Pb(OH)_2;$$

sodium $C_2H_6NSO_3Na$ and *calcium* $(C_2H_6NSO_3)_2Ca$ salts are crystalline and soluble; the *cadmium* salt $(C_2H_6NSO_3)_2Cd$ is a sparingly soluble white powder, and *mercury* salt $(C_2H_6NSO_3)_2Hg$ is insoluble in cold and sparingly soluble in hot water and is well adapted for the preparation of pure taurine and for its detection (Lang, Ber. 1876, 9, 853; Bull. Soc. chim. 1876, [ii.] 25, 180)

Derivatives. *Ethanesulphonimide* or *anhydrotaurine*  $C_2H_4\left<\begin{matrix}NH\\|\\SO_2\end{matrix}\right.$ obtained by the action of ammonia on *β*-chloroethylsulphonic chloride is a gum-like solid, m.p. 45°–50°; is not decomposed on heating with water at 150°, and yields a mercury derivative  $\left[C_2H_4\left<\begin{matrix}N\\|\\SO_2\end{matrix}\right.\right]_2Hg$ with HgO (James, Chem. Soc. Trans. 1886, 49, 486).

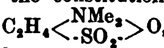
The mono-, di- and tri-substituted taurines are obtained by heating the amine salt of *β*-chloroethylsulphonic acid with the necessary quantity of the amine at 160° in a sealed tube for 10 hours.

Methyltaurine $NHMe{\cdot}C_2H_4{\cdot}SO_3H$, m.p. 241°–242°, forms lustrous prisms belonging to the anorthic system; *ethyltaurine* $NHEt{\cdot}C_2H_4{\cdot}SO_3H$ rhombic prisms, m.p. 147°; *allyltaurine*

$$NH(C_3H_5)C_2H_4{\cdot}SO_3H$$

rhombic prisms, m.p. 190°–195°; *phenyltaurine* $NHPh{\cdot}C_2H_4{\cdot}SO_3H$, thin silky leaves, m.p. 277°–280° (decomp.). *Dimethyltaurine*

$$NMe_2{\cdot}C_2H_4{\cdot}SO_3H,H_2O$$

darkens at 270°–280° and finally decomposes; *diethyltaurine* $NEt_2{\cdot}C_2H_4{\cdot}SO_3H$, m.p. 151°; *methylphenyltaurine* $NMePh{\cdot}C_2H_4{\cdot}SO_3H$. *Trimethyltaurine* is an analogue of betaïne and probably has the constitution represented by the formula  $C_2H_4<\begin{matrix}NMe_2\\{\cdot}SO_2{\cdot}\end{matrix}>O$, since it yields pure trimethylamine when boiled with excess of baryta, and does not give any trace of methyl iodide on heating with hydrogen iodide; it crystallises in rhombic plates that remain unchanged at 300° (James, Chem. Soc. Trans. 1885, 47, 367; 1886, 49, 486; Dittrich, J. pr. Chem. 1878, [ii.] 18, 63). *Taurocyamine*

$$NH{:}C(NH_2)NH{\cdot}C_2H_4{\cdot}SO_3H$$

obtained by heating taurine and cyanamide at 100°–120° forms soluble white prisms, m.p. 224°–226°; *methyltaurocyamine*

$$NH:C(NH_2)NMe{\cdot}C_2H_4{\cdot}SO_3H,H_2O$$

similarly formed from methyltaurine crystallises in large monoclinic prisms that become anhydrous at 110° and turn brown at 285° (Dittrich, *l.c.*). *Phenyltaurocyamine* forms glistening leaves that do not melt at 300°; *dimethyltaurocyamine* $(CH_3)_2(CN{\cdot}NH_2)C_2H_4{\cdot}SO_3H$ has m.p. 248° (decomp.) (James, Chem. Soc. Trans. 1885, 47, 367).

Taurine condenses with benzoic and with phthalic anhydride to form the *compounds* $C_{15}H_{20}N_2S_2O$, m.p. 175°, and

$$C_{25}H_{29}N_2S_2O_{16},7H_2O\ (?),$$

m.p. 50°, respectively (Tauber, Beitr. chem. Physiol. Path. 1903, 4, 323).

Taurocarbamic acid, a-carbamido-β-ethanesulphonic acid, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H$ occurs in the urine after the administration of taurine, and probably also in normal urine. The potassium salt is readily prepared from taurine and potassium cyanate (Salkowski, Ber. 1873, 6, 1191). The acid is also prepared by oxidising ethylenepseudothiourea with bromine water (Gabriel, *ibid.* 1889, 22, 1142); or by condensing taurine with urea in the presence of barium hydroxide (Lippich, *ibid.* 1908, 41, 2068).

Taurocarbamic acid forms prismatic crystals that begin to decompose in a closed tube at 160°, the mass again becoming crystalline and melting at 300° with decomposition. M. A. W.

TAUROCHOLIC ACID $C_{26}H_{45}NO_7S$ occurs in the form of its sodium salt as one of the chief constituents of the bile salts. It yields taurine and cholic acid on hydrolysis; and has been synthesised by condensing the azide of cholic acid $C_{23}H_{39}O_3{\cdot}CON_3$ with an alkaline solution of taurine (Bondi and Müller, Zeitsch. physiol. Chem. 1906, 47, 499; compare Tauber, Beitr. chem. Physiol. Path. 1903, 4, 323), *v.* BILE.

TAXINE $C_{37}H_{52}NO_{10}$ (?) is an alkaloid which is supposed to form the poisonous constituent of the leaves, shoots, and fruit of the yew tree (*Taxus baccata* (Linn.)). It was discovered by Lucas (J. 1856, 550; Arch. Pharm. 1857, 85, 145), but was first prepared more or less pure by Marmé in 1876 (Hilger and Brande, Ber. 1890, 23, 464). It may be obtained by extracting the powdered leaves and seeds with ether or hot alcohol, and after distilling off most of the latter, treating the residue with dilute acid and then precipitating with ammonia, the last two processes being repeated until the product becomes colourless. A better yield is said to be obtained by extracting the leaves, &c., with water acidified with sulphuric, tartaric, or oxalic acid (Vreven, Pharm. J. 1896, 4, 215; Sauvan, *ibid.* 177; Thorpe and Stubbs, Chem. Soc. Trans. 1902. 874; Moss, Sci. Proc. Roy. Dublin Soc. 1909, 12, 92. *See* also Amato and Capparelli, Gazz. chim. ital. 10, 349; Marmé, Chem. Zentr. 1876. 166).

From two specimens of the leaves of a female Irish yew, Moss obtained 0·323 p.c. and 0·623 p.c.; from the seeds of the fruit of the same, 0·079 and 0·082 p.c.; whilst from the leaves of a male specimen he obtained 0·082 p.c. The fleshy part of the berries, however, contained no taxine. In the common yew, both male and female, Thorpe and Stubbs obtained about 0·18 p.c. taxine.

Taxine is a dull, white, amorphous powder, m.p. 82° (slight decomposition). By microscopic examination, Moss detected signs of softening at 60°. It is odourless, has a very bitter taste, is almost insoluble in water, and in light petroleum, but is readily soluble in ether, alcohol, acetone, chloroform, or benzene, also in dilute acids and to a slight extent in excess of ammonia. When heated in a glass tube, a white cloud appears and drops of oil condense and then solidify on the cool parts of the tube. When treated with hydrochloric acid, it decomposes readily (Thorpe and Stubbs, *l.c.*; Moss, *l.c.*). With sulphuric acid it gives a brown to purplish-blue colour; whilst if nitric acid is present the colour is a very deep pink. With reagents generally it gives the characteristic alkaloid reactions. When heated with soda lime, ammonia is evolved. Taxine forms a series of soluble salts with acids and characteristic double salts with a number of metallic salts.

Taxine depresses the action of the heart in frogs, rabbits, cats and dogs. It interferes with the respiration and causes death in a short time through suffocation.

Taxicatin $C_{13}H_{22}O_7$, an inodorous slightly bitter substance, m.p. 166°–167°; when combined with 2 molecules of water its m.p. is 165°; $[a]_D - 72{\cdot}9°$; is also found in *Taxus baccata* (Lefebvre, J. Pharm. Chim. 1907, 26, 241).

TCHA-LAN. A blue powder containing copper; used by the Chinese for obtaining a blue colour on porcelain (Ebelmen and Salvétat, Ann. Chim. Phys. [iii.] 35, 338).

TEA. This term is usually understood to signify both the dried leaves of certain plants belonging to the natural order *Ternstrœmiaceæ* (notably two species of *Thea—T. chinensis* and *T. assamica*, or of hybrids between these two); and also the aqueous infusion prepared from them.

Tea has been used in China for many centuries. Reference to it is said to have been made by a Chinese writer who lived 2700 years B.C. as well as in poems edited by Confucius, about 500 B.C. It appears at first to have been used only medicinally, but Yo Lu, a writer who lived during the latter part of the Tang dynasty, which lasted from 618 to 906 A.D., says that it was drunk in the sixth century, and that during the eighth century it became so common that a tax was levied on it. Arab writers speak of it in China in the ninth century, and it seems to have been introduced into Japan in 810, where its cultivation was commenced early in the thirteenth century. There was no knowledge of tea in Europe until after 1517, when intercourse began between Portugal and China. It was first brought to Europe in 1610 by Dutch merchants, and some years later was introduced into England. A Mr. Wickham, the agent of the East India Company in Japan, wrote to an officer-friend named Eaton, in 1615, asking for 'a pot of the best sort of chaw' (tea), and in Mr. Eaton's own accounts occurs the item, 'Three silver porringers to drink chaw in.' Pepys mentions having tasted it, and writes in his diary, 28th September, 1660, 'I did send for a cup of tee (a China drink), of which I had not drank before,' and, June 28th, 1667, 'Home and there find my wife making of tee, a drink which Mr. Pelling the Potticary tells her is good for her cold and defluxions.' The East India Company presented 2 lbs. of tea to Catherine, the Queen of Charles II., in 1664, and in 1669 they imported it directly from China. Garway, the first tea-dealer in London, issued in 1659 a broad-sheet headed, 'An exact description of the growth, quality, and virtues of the leef of Tea.' In 1660 he bought a lot, and sold it according to quality at from 15*s*. to 50*s*. per lb. He had the infusion 'made according to the directions of the most knowing merchants and travellers into those Eastern countries.' Much prejudice had to be overcome, however, before tea became a popular beverage in England, owing to the fashion of tea drinking being a foreign one, and Jonas Hanway, one of the leading opponents of the new custom, describes it, in his Essay on Tea, published in 1707, as 'pernicious to health, obstructing industry and impoverishing the nation.' In 1666, there were not more than 100 lbs. of tea brought to Europe, and its price was as high as 60*s*. per lb., but about ten years later, the quantity imported from China by the East India Company had reached nearly 5000 lbs. By 1725, the price had fallen to from 13*s*. to 20*s*. for black tea, and to from 12*s*. to 30*s*. for green tea. In 1745 the amount brought to England alone was 730,000 lbs., and in 1800 the infusion had become a very general beverage in this country. The following table gives some idea of the growth of the consumption of tea in the British Isles during the last century :—

Year	Amount consumed (lbs.)	Amount per head of population (lbs.)
1800	23 million	1·4
1850	51 „	1·8
1860	77 „	2·6
1870	118 „	3·7
1880	158 „	4·5
1890	194 „	5·0
1900	250 „	6·0
1910	287 „	6·3
1912	296 „	6·4

The reduction of duty has no doubt aided this rapid increase. From about 1833, when the monopoly of the East India Company was withdrawn, the high duty of 6*s*. or 8*s*. per lb. was gradually reduced until in 1865 it was 6*d*. per lb. Mr. Goschen reduced it to 4*d*. in 1890, since when it has varied between 8*d*. in 1904, to 5*d*. per lb., which is the duty at the present time (1913).

China and Japan were formerly the only great tea-producing countries, although the plant was known as far back as 1780 to be growing in India. In 1788, Sir Joseph Banks pointed out the advantages that would follow from the cultivation of tea in India, and in 1820 Mr. David Scott sent leaves to Calcutta from wild tea-plants growing in the districts that Sir J. Banks had named as suitable for tea-planting; but owing to some doubt as to the true character of the leaves no action was taken in the matter.

Mr. C. A. Bruce noticed the tea-plant growing wild in the jungles of Assam, and in 1839 he received a gold medal from the Society of Arts for this discovery, and for successfully growing and preparing China tea in India. Mr. Bruce's right to this medal was disputed by Captain Charlton, who said that he had pointed out the indigenous Assam tea-plant in 1832. The honour of its discovery has also been claimed for Moneram Dewan, a native. Lord William Bentinck, when Governor-General, formed a committee to introduce the cultivation of tea into India; and in 1834 Dr. Wallish admitted that David Scott had been correct with regard to the leaf. The Government committee at first sent to China for seed and for skilled manufacturers, but Captain Jenkins again pointed out the indigenous *Thea assamica*, and this was used for some years.

In 1836, 1 lb. of tea was sent from India to London; in 1837, 5 lbs.; in 1838, 12 small boxes; in 1839, 95 boxes. In 1839 the Assam Tea Company was formed, which in 1840 bought one of the Government tea-gardens that had failed, and the cultivation has been carried on by private enterprise ever since. The Government, however, was not satisfied with the amount of success attained, and a few years afterwards sent Mr. Robert Fortune to China to study the cultivation and manufacture of tea, and to bring seeds and plants thence to India. He found excellent tea grown and made in the Chusan Islands, and in the neighbourhood of Ning-po and of the Temple of Tein-tung, twenty miles inland; but as this was only for home consumption, he determined also to see and get seeds and plants from the districts of the interior, though this was forbidden to foreigners by Chinese law.

In 1849 he took his young tea plants to Hong Kong, and sent them in four different vessels to Calcutta. In April, 1850, he returned to Shanghai and the north to get implements and engage manufacturers to accompany him. Altogether he introduced more than 12,000 plants into India, and went carefully over the chief tea districts there, travelling up the Ganges and beyond Allahabad. The plantations over the principal tea districts there lay about 29° and 30°N. lat. and 78° and 79°E. long. and were chiefly in the neighbourhood of Almorah, situated about 4000 and 5000 ft. above the sea. The principal districts now are: Upper and Lower Assam, Bheel, Cachar, Chota Nagpore, Chittagong, Darjeeling, Dooars, Dehra Doon, Neilgherry, Sylhet, Terai, and Travancore.

Although in India the native plant or a hybrid is now used (*v. Cultivation*), Fortune's introduction of Chinese growers and manufacturers to teach methods to the natives must have greatly aided the Indian industry.

The rapid increase in the amount of Indian tea imported into England may be seen from the fact that in 1857 we received from India only 121,000 lbs., whilst half a century later the amount was over 150 million lbs. In 1889 the supply of Indian tea to the United Kingdom for the first time exceeded that from China, which was also surpassed by Ceylon tea in 1891, and the excess has been maintained ever since, with a corresponding diminution in the importation of China tea.

Many attempts at the cultivation and manufacture have been made in Ceylon. In 1868, the coffee plants were diseased and the crop failed, and attention was therefore turned to the cultivation of other crops suitable to the climate as cacao, cinchona and tea. The latter industry has grown enormously, as may be seen from the table below.

Ceylon tea combines some of the good qualities of Indian and of Chinese tea, and it does not require blending, but it does not keep so well. In this respect Chinese tea is much the best, and it is customary therefore to store smaller quantities of Indian or Ceylon tea than of Chinese. In comparison with Indian tea, Chinese is also more uniform in quality. Some Indian and Ceylon growers are apparently inclined to attend more to quantity than to quality. Our increased importation from India and Ceylon is partly owing to the heavy transit and export duties levied on tea by the Chinese Government, also to the faulty and often objectionable methods of manufacture, chiefly by hand labour, followed in China, as compared with the more scientific methods and almost universal employment of machinery in India and Ceylon.

IMPORTS TO THE UNITED KINGDOM
(In million lbs.).

—	China	India	Ceylon	Other countries	Total
1873	135	20	(23 lbs.)	8¾	163¾
1875	170	26	(1400 „)	1½	197½
1880	158¼	45½	(150,000lbs.)	3¼	207
1885	140	64¾	3¾	4	212½
1890	69¼	100½	47	6¾	223½
1895	40	123½	83½	8½	255½
1900	21½	153½	114½	9½	299
1905	7¾	179	106¼	15½	308½
1910	19	180¼	107½	25	331¾
1912	20½	192½	112½	35½	361

From the above table it will be seen that, the rapid increase in the imports of Indian and Ceylon tea was arrested during the period 1905–1910, whilst the importations from China and other countries showed a marked tendency to increase. This is due partly to the fact that Indian tea is gradually displacing China tea in markets such as Russia, the United States, and Canada, hitherto favourable to the teas of China and Japan, so that the supply of Indian tea is at present barely equal to the demand. In Ceylon, moreover, a considerable amount of tea has, in recent years, gone out of cultivation for the more profitable cultivation of rubber. Also, the Chinese have been making strenuous efforts to regain some of their lost trade by fiscal changes and by attention to improved methods of cultivation and manufacture. The returns for 1912 showed a revival of the Indian and Ceylon tea trade with the United Kingdom.

The European nations who consume most tea are Great Britain, Holland, and Russia. Next to Great Britain, the United States import more than any other country, but reckoned by the amount drunk per head the people of Australia and New Zealand are the greatest tea-drinkers in the world. The following table shows the amount of tea consumed per head per annum in the principal tea-drinking countries:

Australia and New Zealand	6·8 lbs.	Russia .	. 1·3 lb.
United Kingdom	6·4 „	United States	1·1 „
Canada .	. 4·5 „	Persia .	. 0·8 „
Netherlands	. 1·7 „	Chile .	. 0·7 „
		Argentina	. 0·6 „

Europe is supplied chiefly by China and India, and North America by Japan; but China black tea and Japan green tea are being rapidly supplanted in Canada and the United States by Indian black and Ceylon green tea respectively.

The methods of making the infusion vary in different countries. In China a pinch of tea is put into the cup, boiling water is poured on it, and the infusion is drunk at leisure, even after it is cold, and without milk or sugar. The water to make it is got from a running stream if possible, otherwise from a spring, *not* from a well, and is boiled slowly. The methods prevailing in Japan are described further on. In England the old fashion of letting the tea 'brew' and constantly adding hot water to the same leaves, is dying out; and the best tea makers pour boiling water on to the leaves, which have been put into a heated pot, let it stand on them for about five minutes, and then pour off the infusion or take out the leaves. The reason for this method is, that by that time, most of the theine and essential oil but not more than a third of the astringent tannin have been extracted. In Russia, lemon-juice is added to the infusion. In Germany, rum is sometimes added, as well as cinnamon or vanilla. In Spain, lemon-verbena leaves are added.

Botany. The tea-plant (*Thea assamica* or *Camellia Thea*) belongs to the order *Ternstrœmiaceæ*.

Leaves. Lanceolate, serrate, acute, and thick. They are alternate, and their stalks are short. Their upper surface is green and glabrous, and their under surface sometimes hairy on the nerves. The veins from the midrib go nearly to the edge, and then unite to form an intra-marginal vein. The leaves are dotted with pellucid oil glands, and numerous unicellular hairs are found on the under surface, especially of young leaves. The hairs, after emerging from the epidermis, bend suddenly at a right angle in a direction parallel to the surface of the leaf, and are very characteristic. The stomata are very numerous and are bordered by two special cells of reniform shape. Stellate crystals of calcium oxalate occur in the internal tissues or mesophyll, as well as thick-walled sclerenchymatous cells of very irregular shape giving support to the upper and lower layers of the leaf, and known as 'sclerites' or 'idioblasts.' These serve to distinguish tea from most other leaves likely to be used for the purpose of adulteration.

Flowers. White or slightly yellow, or rose tinted, axillary, regular and hermaphrodite. Bracts, two or three below the calyx. There are five round and convex sepals, and five obovate obtuse petals (more rarely, six or more). The stamens are indefinite, monadelphous, and adhere to the petals by their base. The styles are three in number, with simple stigmas. The ovary is superior and three-celled, each cell containing from four to five pendulous anatropous ovules.

Fruit. Woody, forming a three-celled loculicidal capsule, which remains green for a long time. Each cell contains one exalbuminous seed, the remaining ovules never ripening.

Cultivation. Our chief authority on the cultivation and manufacture of tea in China is

Robert Fortune, who in his Journey to the Tea Countries of China gives many interesting particulars about the cultivation and manufacture of tea, and of his adventures in getting to the interior disguised as a mandarin.

He states that the parts of the world best suited by climate for the cultivation of the tea plant are China, Japan, India, Ceylon, South America, parts of Australia, the shores of the Mediterranean, the middle of France, and even Ireland. Java is now one of the chief tea producing countries, and amongst other countries where tea is more or less successfully cultivated at the present time may be mentioned Burmah, the Straits Settlements, Natal, Nyassaland, Mauritius, Queensland, the Fiji Islands, Brazil, and the Caucasus.

A warm climate is essential. In the best districts in China the ordinary range of the thermometer in the summer at 3 P.M. is between 80° and 90°F.; it sometimes reaches 100°, and it rarely falls below 32° in winter.

The best position for a tea-plantation, if other conditions are favourable, is a slope facing the south, because on sloping ground there is natural drainage, and the soil does not get too wet; it ought never to be as wet as in rice fields. If flat ground is used, the tea-gardens are often artificially raised, and are always carefully drained. The spring rains are most beneficial, provided the drainage be efficient. There must be a constant supply of water, either from natural sources or by irrigation. Hilly districts are suitable, because the vegetable matter washed down from above enriches the gentler slopes and the level ground below. Increased altitude (within limits) appears to improve the flavour of tea, but with a diminution of the quantity of leaf produced. The plant flourishes best in rich loam mixed with sand and gravel. Oak-bearing land is considered extremely good for tea plants.

The seed—which is in appearance like a hazel nut, having an outer and an inner shell inclosing a kernel, and ripens about a year after the flower has faded—is gathered in October, and kept in sand and earth, in which it germinates, until March, when it is sown in rows. Holes are dug and left for about two weeks, then filled with surface soil, and three seeds are put into each hole about six inches apart. The best plant remains in the hole, and the others are transplanted to vacancies. The plants are about 4 ft. apart, and the same distance separates the rows. About 26 lbs. of seed are required for an acre, yielding about 2500 shrubs. Sometimes the seeds are sown more thickly in corners of the tea-farm or in nurseries, and the plants transplanted when a year old at the beginning of the rainy season.

The wild plant (originally, probably, the *Thea assamica* of the forests of Northern India) may grow to a height of from 30 to 50 ft., but the cultivated plants are pruned and kept to a height of from 3 to 6 ft., so that they become well-spread, bushy shrubs resembling somewhat the 'Portugal laurel' in appearance. The leaves are not picked until the plant is three years old. It does not yield its full quantity until its sixth or seventh year, and in China leaves are seldom gathered from a plant more than twelve years old. A good cultivator takes care that some portion of his farm shall be resown every year.

In India, only those plants are allowed to *flower* which are to be kept for producing seed, the leaves of which are not to be made use of. Fortune introduced Chinese seed into India; but it has been found that the indigenous plant, or a cross between it and the Chinese varieties, yields better tea in India. The Chinese plant makes the best green tea, whilst hybrids are best for black. Only such seeds as are used in India are imported into Ceylon.

The raw leaves yield only about one-fifth of their weight of manufactured tea. The plants give in their third year not more than a *maund* (80 lbs.), but in their fifth year about 280 lbs. of tea per acre. The amount increases from the fifth to the twelfth year, but varies greatly in different districts, and it also depends on the plucking, whether 'fine' or 'coarse.' In the richest years, the amount in some places (*e.g.* Sylhet) may reach 1000 lbs. per acre. A tea bush from 8 to 12 years old will yield ¼ lb. of manufactured tea, and taking 2500 bushes per acre, the average yield in India is thus over 600 lbs. per acre.

Manufacture. The two great classes of tea are *green* and *black*, the differences between them depending solely on the mode of manufacture. Sub-divisions depend on the *age of the leaves*, *i.e.* the time of the year they are gathered, and the *way they are rolled*.

The chief sub-divisions are as follows:—

Green Varieties.

Hyson. Leaf-buds and first leaf; picked in April. The young leaves, which are very uniform in size, are carefully twisted and rolled longitudinally into a spiral form.

Skin Hyson consists of the inferior leaves of hyson rolled transversely and longitudinally and frequently enclosing the débris of other green teas. It is often merely tea refuse, and the coarser kinds are known in the vernacular as 'tea bones.'

Gunpowder. According to Dujardin-Beaumetz, this is simply carefully selected hyson. According to Johnston and Church, it is from a special plantation, and flavoured with *Olea fragrans*, the sweet-scented olive. The leaves are cut transversely in three or four parts before being rolled into pellets.

Pearl or *Imperial.* Dujardin-Beaumetz describes this as a kind of hyson, but coarser than the true hyson, and of a silver-green colour. Johnston and Church say that the true Imperial, which is excellent, is rarely sent to Europe, and that what we call 'Imperial' is a tea from the Chusan Archipelago flavoured with the *Olea fragrans*. The tea occurs in the form of pellets made by rolling the leaves first longitudinally, then transversely.

Black Varieties.

The different kinds of black tea are usually classified according to the age of the leaf. The youngest leaves give the best tea, and the order, commencing with the youngest when plucked, is as follows:—

(*a*) *Flowery Pekoe* (*b*) *Orange Pekoe* (*c*) *Pekoe*	'Poco' refers to the white down of the young leaf.

(*d*) *First Souchong* } 'Souchong' means
(*e*) *Second Souchong* } 'small plant.'

(*f*) *Congou.* 'Congou' means 'labour,' and is intended to express the great care required in the preparation of this tea. (*a*) (*b*) (*c*) mixed make *Pekoe*; (*d*) and (*e*) mixed with *a, b, c* give *Pekoe-Souchong.*

Pekoe. Youngest leaf and leaf-buds; picked in April. This is sometimes flavoured by the addition of orange, rose, or jasmine flowers. When with the first-named, it is called *Orange Pekoe.*

Souchong. The strongest and perhaps finest of the black leaf teas. It consists of the larger of the young leaves, and is suitable for use either alone or in blends.

Congou. The younger leaves from the third crop, older and larger than *Souchong.* This constitutes the ordinary beverage of the inhabitants of China and Russia.

Bohea. The commonest variety of tea, consisting of the older leaves of the third crop or a mixture of various leaves, stalks, and dust.

Caper (plain-scented). Various teas or tea dust made into hard grains by means of gum or rice-water, sometimes polished with graphite or coloured with indigo, &c.

Broken Pekoe. Siftings of various Pekoes.

Fannings. Siftings of Congou.

There are other special varieties of teas as Twankay (green), Kaisow (red leaf), Moning and Oolong (black, with more or less of the flavour of green), used chiefly for giving 'life' to blends.

The leaves are plucked three times a year. In April (that is in China just before the spring rains); at the end of May or beginning of June; and towards the end of June, or, according to some authorities, in July. Sometimes there is a fourth gathering in the late summer or early autumn, but leaves of such a size and age as they are then make only the common and coarser kinds of tea. In South Australia there are always four, and sometimes in wet seasons a fifth gathering. Women are generally, if not always, employed in India, and sometimes in China, for the picking.

The plants are picked as successive 'flushes' appear, a 'flush' being the throwing-out of new shoots and leaves; and the number of flushes in a season—that is, in from seven to nine months—varies from 18 to 25, according to the soil and climate. In Ceylon, the flushing continues all the year round. Up to a certain point the more a plant is picked the more new shoots it throws out. At the end of the season each shrub is 3½ or 4 ft. high, and about 5 ft. in diameter. It is then pruned down to a height of 2 feet and a diameter of 3 ft., and thus it remains until the spring.

In the manufacture of *green tea* the object is to keep the colour and prevent fermentation; it is necessary, therefore, to roast as soon as possible after picking, and finish the whole process quickly.

In the manufacture of *black tea*, on the contrary, the leaves are dried slowly before manipulation, and one of the processes is that of fermentation (*cf.* Eighth Int. Cong. Appl. Chem. 1912, Sect. VIII.).

Processes of manufacture of green tea.
Chinese methods.

The methods and apparatus employed in China are very simple and primitive. The tea farms are very small, seldom exceeding five acres, and almost every cottager grows sufficient tea to supply the wants of his family and possibly secure other necessaries of life by selling the surplus to the travelling tea-merchants who periodically visit the country districts for that purpose.

The principal processes are as follows:—

Steaming. To get rid of the raw flavour, and preserve the colour, the leaves are spread out in bamboo trays and fitted into a bamboo box, the bottom of which is a boiler. Here the leaves remain for an hour or two. They then are exposed on tiled floors, or in shallow bamboo trays out of doors in the shade, to prevent their turning yellow and becoming hard and brittle by drying too rapidly as they would if placed in the sun, and are meanwhile separated from stalks and dirt.

Roasting. Half a pound of leaves at a time is put into a *kno* or iron pan, 10 ins. deep and 16 ins. in diameter, which is set in a brick stove over a brisk wood fire. Here the leaves are kept 4 or 5 minutes, and stirred rapidly with the hand. When taken out they are moist and flaccid, although much vapour has been given off.

Rolling. The object of this is to break the cells, contents of which come out and spread over the surface of the leaf, so that a fine aroma is produced. This is done on the rattan table, where the leaves are rolled by hand into balls, shaken out again, and rolled once more, passing from hand to hand until they reach the head workman, who sees whether they have the proper twist. If they are right they are shaken out on flat trays or sieves, and allowed to cool for a few minutes.

The second roasting is done over a slow charcoal fire for an hour or an hour and a half, at the end of which the green colour is fixed, dull at first, but gradually growing brighter. During the second roasting one man moves and occasionally rolls the leaves, while another fans.

Sifting. This is first done by means of sieves of different sizes; then the leaves are winnowed on large bamboo trays, and finally they pass through the winnowing machine. This gets rid of dirt and impurities, and separates the different kinds of tea, according to size and twist of leaf.

During the sifting the leaves undergo a *third roasting* or *re-firing.* It was about 5 minutes before the end of this last roasting that the manufacturer used to add the Prussian blue, &c., for colouring. This was done for the foreign market only, as this highly coloured tea was prized in Europe until it was discovered to be faced. The whole manufacturing process takes about 10 hours. Sometimes the sorting and re-firing take place at Canton before exportation instead of in the interior.

Japanese methods.

The principal kinds of Japanese green tea are Gyokuro and Sencha, which are those chiefly used by the Japanese themselves, and exported to the United States of America, Canada, and Australia.

The methods of manufacture are very much the same as in China, but whilst machinery is now almost universally employed in Japan for teas intended for exportation, yet owing to a prevalent idea that the use of machinery is detrimental to the development of the finest aroma, the superior qualities of tea are still prepared by the old-fashioned hand processes.

Indian methods.

Machinery is used almost exclusively in India for the manufacture of tea, as insuring 'more cleanliness and uniformity' than the method by hand. Each process appears to be gone through once without necessity for repetition.

There seems to be less difference between the Indian and the Chinese mode of manufacturing green tea than there is between the methods of the two countries in making black. The Indian method of making green tea is as follows:—

The leaves are picked twice a day. Those which are brought in at 1 p.m. are partly manufactured the same day; those which come in at night are spread six inches thick until next morning. The various processes are:

1. *Drying* (if necessary).
2. *Roasting.* This is done in pans over fires until the temperature is 160°F., and the leaves are meanwhile vigorously stirred for seven minutes.
3. *Rolling.* This is done four times in succession, the leaves being dried in the sun between each rolling.
4. *Second roasting.* The leaves are returned to the pans, and roasted at the same temperature as before.
5. *Beating.* Bags are filled with the leaves, which are then beaten heavily. They remain in the bags all night.
6. *Third roasting.* During the stirring this time the temperature gradually falls from 160°F. to 120°F.
7. *Sifting and sorting.* The sieves are round and made of brass wire or cane, with wooden sides 3½ ins. high. Before sifting, any red leaves there may be are carefully picked out.

The method of manufacture in *Ceylon* is the same as that in India.

Processes of manufacture of black tea.
Chinese methods.

A little of the soft stalk is picked with the young leaves and leaf-buds for black tea.

Withering. The leaves are spread on large bamboo trays or mats, and exposed out-of-doors for some hours. If leaves are gathered during the wet season, this first drying takes place indoors on frames standing some feet above pans of hot charcoal. This process renders the leaves soft and pliable; the stalks bend without breaking, and do not crackle when compressed.

Tossing and fermentation. In a cool building, or in the shade out-of-doors, the leaves are then tossed and gently patted till they are soft and flaccid. They then lie in heaps, covered with a cloth, and are carefully watched until they get a slightly reddish tinge, and give out a fragrant smell.

First roasting and rolling. This roasting is for 5 minutes in shallow iron pans over wood fires. The rolling is on rattan tables, the same as for green tea. Sometimes the rolling takes place first, and sometimes the roasting.

Exposure out-of-doors. The leaves are now shaken out thinly on sieves, and put out-of-doors on bamboo frames for about 3 hours. In the black-tea districts they are seen in front of all the cottages; and workmen go from one to another turning and separating the leaves. The day should be fine and dry, but not too hot. When dry enough, they are removed to the factory.

Second roasting and rolling. This roasting is in the same shallow iron pan as before, and the rolling on the same table.

Drying and rolling. The leaves are spread to a depth of about 1 in. in sieves, and these are put into tubular baskets called poey-longs, which are slightly contracted in the middle, and are 2½ ft. long and 1½ ft. broad, somewhat like a dice-box in shape. There are cross-wires a little above the contraction of each basket on which the sieve stands. The poey-long, the mouth of which is covered by a bamboo tray, stands upright over a low stove built on the ground, and containing a small quantity of charcoal, so that the tea-sieve is about 14 ins. above the stove. These stoves are built round three sides of a long narrow room, and are 2 or 3 feet deep, and 5½ ins. high. While the rolling goes on, the balls of leaves are left standing in heaps until all are done. The drying and rolling go on alternately, either two or three times, until the leaves are dry and crisp and have the right dark colour.

Sifting. This is done by means of large circular bamboo trays, and the large leaves, if necessary, are picked out by hand.

Final drying. The fires are covered to reduce the heat. The leaves are placed much more thickly in the baskets, and the workman makes a hole with his hand through the centre of those in each sieve, to equalise the heat and allow the charcoal vapours to escape. Here the leaves remain over a slow fire for 2 hours or longer. The mouth of the basket is quite closed by a tray. For home consumption in China tea is not dried quite so much, and it is kept for a year before use.

Japanese methods.

The manufacture of black tea in Japan has not hitherto been very successful, owing probably to imperfect fermentation, a process to which the native leaf does not appear to be so well adapted as the China leaf.

The mode of manufacture is the same in principle as that of China, but differs in the order of the processes and the time of their duration.

Large quantities of tea of the Oolong variety are shipped from Formosa. This, although similar in appearance to black tea, has the flavour of green tea.

All teas in Japan are re-fired in the 'godowns' of the exporters. This is to drive off any excessive moisture, tea being extremely hygroscopic, and to destroy any germs which might, especially in the presence of moisture, cause the tea to decay on its voyage to other parts of the world. According to Kozai, the amount of moisture in ordinary Japanese tea is from 10 to 11 p.c., but it is reduced by re-firing before exportation to 3 or 4 p.c.

It has been proved by experiments with leaves of other plants in Japan that steaming not only preserves their colour but prevents fermentation. This may be because the heat of the steam destroys the enzymes which produce fermentation. Hence, for black tea, the leaves must on no account be steamed, but withered, and then allowed to ferment. For green tea the leaves are steamed to prevent fermentation and preserve colour, and are manufactured quickly.

In Japan, other kinds of tea are manufactured exclusively for home consumption called respectively *bancha kamairii* or *pan-roasted tea* and *yencha* or *flat tea.* The former is a very inferior tea consisting of old leaves from the last year's crop mixed with broken stalks and twigs. Kamairii is made simply by alternate roasting in an iron or bronze pan, and rolling on a table seven or eight times over. Until 250 years ago all tea was made so, but now it is rare. According to Y. Kozai this is sometimes made in China, and is known there as '*sencha*' (*v. supra*). For *flat tea* the leaves are supplied from a special plantation. They are not rolled or touched by the hand at all, but are spread on stiff paper for firing by means of bamboo sticks, and are alternately collected and spread out until nearly dry. Then they are taken from the furnace, all the broken or yellow leaves removed, and fired again. The final drying lasts all night at a gentle heat, and the leaves are then separated into three classes. For use they are ground to a powder of the fineness of flour, drunk with the infusion. This tea ('yencha') is usually reserved for ceremonial occasions.

Indian methods.

The processes are as follows:

1. *Withering* on fine basket-work trays in the sun.

2. *Rolling.* This is done either by the rolling machine or by a line of men on each side of a table, who pass the leaves from one end to the other. When soft and 'mashy,' and giving out juice, the leaves are made into a ball, the juice that has come out being mopped up constantly during the process.

3. *Fermentation.* The balls stand until fermented, and are most carefully watched, as the flavour and quality of the tea depend largely on stopping this process at the right moment, and only skilled tea-makers can judge of this. At the proper time the balls are broken up, and the leaves spread thinly on mats in the sun. When they get rather black they are collected and re-spread, so that all the leaves may be alike, but this does not take long, for

4. *Drying or Firing* should take place as quickly as possible after the fermenting process, to drive off all the moisture. This is generally done in a chest of firing drawers, which consists of a set of trays one above the other, the bottom of each, on which the leaves are spread, being made of fine wire gauze, so that all the trays can be heated at once. Formerly charcoal fires always produced the heat, but now hot air is often used instead. When the tea comes out of this machine it is almost black, and has a very delicate aroma.

5. *Sorting.* In sieves to separate the leaves into the different kinds for commerce.

Chemistry of tea. The analyses of air-dried tea differ according to whether the tea be green or black, where it has been grown, and other circumstances.

The most important constituents of tea are caffeine (theine), tannin, ash, and essential oil. Of these it is generally found that there is rather more caffeine in black tea than in green, and more tannin in green (though this rule is not without exceptions); the amount of ash is fairly constant; the quantity of essential oil is very small in both, but it seems to be larger in green tea than in black. The total matter soluble in hot water is also larger in green tea than in black.

A valuable paper by Y. Kozai (Researches on the Manufacture of Various Kinds of Tea: Bulletin No. 7 of the Imperial College of Agriculture and Dendrology, Japan) gives analyses of the tea-leaves (all of the same kind) from a certain plantation under three different conditions:—

1. Dried at 85° C.
2. Made into green tea.
3. Made into black tea.

The following are the results:—

—	Original leaves dried	Same made into green tea	Same made into black tea
Crude protein . .	37·33	37·43	38·90
Crude fibre . .	10·44	10·06	10·07
Ethereal extract .	6·49	5·52	5·82
Other nitrogen-free ext.	27·86	31·43	35·39
Ash	4·97	4·92	4·93
Caffeine . . .	3·304	3·200	3·300
Tannin (calculated as gallo-tannic acid) .	12·91	10·64	4·89
Soluble in hot water .	50·97	53·74	47·23
Total nitrogen . .	5·973	5·989	6·224
Albuminoid nitrogen .	4·107	3·937	4·106
Caffeine nitrogen .	0·956	0·926	0·955
Amino nitrogen . .	0·910	1·126	1·163

100 parts of dried leaves yielded:—

Green tea	98·64
Black tea	95·47

From the above figures it follows that in the process of manufacture the change in the amounts of the various constituents was such as is shown in the following table, where (+) denotes the gain, (−) the loss in 100 parts of each constituent:

	Green tea	Black tea
Dry matter . . .	− 1·36	− 4·56
Crude protein . . .	− 1·70	− 0·61
Crude fibre . . .	− 4·98	− 7·94
Ethereal extract . .	−16·18	−14·33
Other nitrogen-free extract	+11·31	+21·21
Ash	− 2·42	− 3·01
Caffeine	− 4·49	− 4·92
Tannin	−18·67	−63·82
Soluble in hot water .	+ 5·96	−11·69
Total nitrogen . . .	− 1·08	− 0·61
Albuminoid nitrogen .	− 5·57	− 4·58
Caffeine nitrogen .	− 4·49	− 4·92
Amino nitrogen . .	+22·75	+22·42

The loss in ethereal extract is considerable, because part of the tannin changes during manufacture to a form insoluble in ether. In black tea, however, which undergoes fermentation, acids are formed during the fermentation that are soluble in ether.

The slight loss of ash and of caffeine arises from the mechanical loss of sap during manufacture.

The loss of tannin occurs during the heating processes in the manufacture of both kinds of tea. In black tea there is loss also during fermentation, when the tannin decomposes into substances *insoluble* in hot water. This accounts for the fact that hot water extracts less tannin from black than from green tea, and to this is no doubt largely due the preference given in the United Kingdom to black tea on the assumption that it is more wholesome than the green varieties.

Altogether, the change from the original leaves is greater in black tea, because of the process of fermentation.

The following are general analyses showing the differences between green and black tea :—

GENERAL ANALYSES (Bell).

	Congou (black)	Young Hyson (green)
Moisture	8·20	5·96
Caffeine	3·24	2·33
Albumin insoluble	17·20	16·83
Albumin soluble	0·70	0·80
Extractive by alcohol containing nitrogenous matter	6·79	7·05
Dextrin or gum	—	0·50
Pectin and pectic acid	2·60	3·22
Tannin	16·40	27·14
Chlorophyll and resin	4·60	4·20
Cellulose	34·00	25·90
Ash	6·27	6·07
	100·00	100·00

ANALYSIS OF SIX VARIETIES OF CHINA GREEN TEA (Geissler).

	Max.	Min.	Average
Moisture	7·78	5·39	6·43
Half-hour extract	44·70	30·20	36·74
Total extract	50·00	43·30	46·56
Insoluble leaf	49·61	44·60	47·05
Tannin	19·11	11·87	14·57
Caffeine	2·86	1·52	2·02
Soluble ash	5·02	2·02	3·28
Insoluble ash	6·38	2·11	3·61
Ash insoluble in HCl	0·66	0·21	0·49

ANALYSIS OF ELEVEN CONGOU BLACK TEAS (Geissler).

	Max.	Min.	Average
Moisture	9·15	7·65	8·37
Half-hour extract	32·14	23·48	28·40
Total extract	37·06	27·48	34·35
Insoluble leaf	63·85	54·50	57·20
Tannin	13·89	8·44	11·54
Caffeine	2·87	1·70	2·37
Soluble ash	3·52	2·28	3·06
Insoluble ash	3·86	1·90	2·68
Ash insoluble in HCl	1·31	0·32	0·425

ANALYSIS OF SIX INDIAN TEAS (Geissler).

	Max.	Min.	Average
Moisture	6·19	5·56	5·81
Half-hour extract	39·66	37·80	38·77
Total extract	45·64	41·32	42·94
Insoluble leaf	53·07	48·53	51·24
Tannin	18·86	13·04	14·87
Caffeine	3·30	1·80	2·70
Soluble ash	3·68	3·24	3·52
Insoluble ash	2·22	1·93	2·12
Ash insoluble in HCl	0·296	0·137	0·178

The results of more recent analyses of various teas from India, Ceylon and China (22 samples) are given on p. 428, the percentages being calculated on the tea dried at 100° C. (Tatlock and Thomson, Analyst, 1910, 108).

The following circumstances affect the chemical composition of tea :—

1. *Age of leaves.* From spring to autumn, the percentage of water, crude protein, and nitrogen free extract continually decreases; the caffeine diminishes gradually; the crude fibre increases proportionally as crude protein decreases. The percentage of ethereal extract increases proportionally as nitrogen free extract decreases. The percentage of tannin increases slightly; that of substances soluble in hot water gradually diminishes at first, then increases slowly. The percentage of *total ash* slightly fluctuates, but the constituents change considerably.

Potash and phosphoric acid diminish, whilst the lime, magnesia, iron, soda, manganese, and sulphuric acid increase.

Silica and chlorine remain nearly constant.

Some of the above general statements are shown more exactly by the following figures :

	May p.c.	November p.c.
Water	76	60
Caffeine	2·85	0·84
Total nitrogen	4·91	2·67
Amino nitrogen	0·66	0·08 (September) 0·01 (following May)
Tannin	8	11 or 12
Ash	4·69	5·14

Probably a portion of the amino nitrogen became caffeine nitrogen.

These results were obtained by O. Kellner in conjunction with K. Oku and K. Ogasawara, of Japan (' Landwirthschaftliche Versuchs-Stationen,' 1886, 370).

2. *Effect of light.* On a plantation of uniform conditions and similar plants, Y. Kozai tried what difference of chemical composition there would be between the leaves of plants grown under the usual conditions and those of plants screened from the light by wooden frames during the last three weeks of their growth before picking. He obtained the following results :—

	Screened leaves	Leaves exposed to light
Caffeine	4·532 p.c.	3·784 p.c.
Total nitrogen	7·835	6·945
Caffeine nitrogen	1·311	1·0943
Tannin	no difference.	

The screened leaves were bleached, and had a fine and peculiar aroma.

Kozai states that there is not actually more caffeine in the screened than in the exposed leaves; but that in the latter there is a preponderance of woody fibre which makes the total dry matter larger.

—	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Country	India	India	India	India	India	India	India	India	India	India	Java	C'yl'n	C'yl'n	C'yl'n	C'yl'n	C'yl'n	China	China	China	China	China	China
District	Assam	Assam	Assam	Assam	Assam	Assam	Darjeeling	Darjeeling	Dooars	Travancore	—	—	—	—	—	—	Moning	Moning	—	O'l'ng	—	—
Grade	Or'ge Pekoe	Pekoe	Broken Tea	Pekoe	Pekoe	Dust	Broken Pekoe	Pekoe	Pekoe	Broken Tea	Negiara	Broken Or'ge Pekoe	Pekoe Souchong	Pekoe	Pekoe Souchong	Pekoe Souchong	—	—	Lapsang Souchong	—	Sc'nted Or'ge Pekoe	Gunpowder
Cost, per lb.	10*d.*	8½*d.*	8½*d.*	8*d.*	6½*d.*	5½*d.*	10*d.*	8½*d.*	8½*d.*	6½*d.*	6½*d.*	1*s.*	11½*d.*	8*d.*	6½*d.*	6½*d.*	1*s.*6*d.*	8½*d.*	1*s.*6*d.*	1*s.*2*d.*	1*s.*2*d.*	9*d.*
Water extract	48·92	49·42	49·75	45·94	45·64	46·84	44·10	43·47	44·85	45·80	44·84	42·15	48·25	46·82	41·32	41·96	43·25	40·72	38·43	46·94	45·47	43·73
Caffeine	3·48	3·59	3·66	3·84	2·81	4·91	2·96	2·78	3·10	3·45	3·40	3·65	4·14	3·53	2·59	2·34	3·75	2·62	3·10	3·12	2·86	2·84
Tannin	14·81	13·57	14·98	14·78	14·76	16·61	13·32	13·87	14·69	14·20	14·48	12·24	13·91	13·21	10·13	12·00	10·90	9·81	10·09	10·94	7·27	8·02
Ash soluble in water	3·63	3·91	3·15	3·55	3·61	2·84	3·60	3·69	3·66	3·70	3·50	2·87	3·27	3·09	2·76	3·04	2·94	2·92	3·61	3·08	3·24	3·15
,, ,, (less silica)	2·10	2·38	1·90	2·69	1·92	2·52	1·80	1·77	2·15	2·08	2·25	2·22	2·01	2·35	2·53	2·28	2·45	2·54	2·09	2·52	2·68	2·98
Silica (chiefly sand)	0·07	0·36	0·17	0·31	0·13	0·46	0·07	0·11	0·09	0·04	0·13	0·05	0·03	0·04	0·03	0·04	0·54	0·65	0·08	0·78	0·08	2·74
Total mineral matter	5·80	6·65	5·22	6·55	5·66	5·82	5·47	5·57	5·90	5·82	5·88	5·14	5·31	5·48	5·32	5·36	5·93	6·11	5·78	6·38	6·00	8·87
Moisture originally present	6·80	5·30	7·26	6·96	8·20	5·94	6·80	6·46	7·16	6·65	7·54	5·96	7·05	5·60	7·54	8·00	8·02	9·06	9·70	7·28	6·12	6·70

3. *Age of plants.* It has been said that old plants make the best tea. This has not yet been thoroughly proved, but researches by O. Kellner with M. Tanaka and B. Minari on plants aged 4, 7, 16, and 20 years respectively, show that the amount of water decreases regularly with the age of the plant, and that all other changes are extremely irregular. The older the plant, the more manuring and pruning is necessary to get a good crop of leaves.

4. *Manuring* appears to have little effect on the chemical composition of the leaves, although it increases the number on each plant. Bush prunings, weeds, and general rubbish make good manure. Animal manure must be used with great care

Theine or *caffeine* may be considered the active principle of tea, physiologically speaking, since it has been found in nearly all of the various plants whose leaves are used for infusions and take the place of tea.

The published determinations of caffeine in tea vary greatly, but this is partly owing to the different methods used.

Determinations of caffeine made in the Inland Revenue Laboratory (Bell's Foods) gave:

Kind of tea	Price per lb. *s.*	*d.*	Percentage of caffeine
Bohea	1	7	3·31
Congou	2	6	2·93
Young Hyson	3	2	4·29
Gunpowder low	2	6	3·18
,, good	5	0	4·93
Assam, low	2	8	3·03
,, good	4	6	4·83

It will be seen that there is no direct relation between the proportion of caffeine and the commercial value of the tea.

Determination of Caffeine in Ceylon and Indian Teas (Paul).

—	Elevation at which grown	Moisture per cent.	Caffeine p.c. Original tea	Caffeine p.c. Dry tea
Ceylon teas.	Feet			
Penrhos	2,500	6·8	4·56	4·89
F. L. C.	—	6·0	4·56	4·85
Nahalma	300	5·6	4·54	4·80
Hairs from leaves	—	6·6	2·40	2·57
Hardenhuish Pekoe	3,500	3·8	4·08	4·24
Woodstock Pekoe Souchong	4,200	3·6	3·44	3·57
Radilla Broken Pekoe	4,800	4·6	4·10	4·30
Morton Pekoe	400	4·2	3·98	4·15
Penrhos Broken Pekoe	2,500	6·4	4·64	4·96
Strathellie Orange Pekoe	2,000	5·4	4·10	4·33
Nahalma Orange Pekoe	300	5·4	4·06	4·29
Venture Orange Pekoe	4,300	5·4	3·74	3·95
St. Leys Pekoe Dust	4,600	5·6	3·46	3·66
Venture Pekoe Souchong	4,300	4·8	3·40	3·57
Venture Broken Orange Pekoe	4,300	6·6	3·98	4·26
Calsay Pekoe Souchong	5,000	6·2	3·22	3·43
Venture Pekoe	4,300	5·6	3·48	3·68
St. Clair Orange Pekoe	4,200	4·6	3·90	4·09
Indian teas.				
Pekoe Tips, picked out	—	7·56	4·27	4·62
Broken Pekoe	—	7·00	4·48	4·81
Pekoe	—	6·40	4·16	4·44
Orange Pekoe	—	4·80	4·66	4·89
Pekoe	—	5·60	4·48	4·74
Broken Pekoe	—	4·80	3·76	3·95
Pekoe	—	5·40	3·66	3·86
'Weak' Tea	—	6·80	4·06	4·35
'Strong' Tea	—	5·80	4·18	4·43
Mixture	—	6·00	3·64	3·87

Estimation of caffeine in tea. Waage has examined 37 methods proposed or used for the determination of caffeine, but gives the preference to that of Mülder with certain modifications. This consists in treating the concentrated aqueous infusion by lime or magnesia, evaporating to dryness and extracting the caffeine with chloroform, ether, or benzene. In some cases the aqueous extract is first treated with lead acetate to remove tannin and colouring matters, the excess of lead being removed by sodium phosphate or hydrogen sulphide.

According to Blyth, low results may be obtained through loss in drying the extracted caffeine by prolonged heating at 100°C., owing to the fact that caffeine sublimes below this temperature.

Tannin. The methods for the estimation of tannin are very numerous. That usually employed is Löwenthal's process as modified by Councler and Schröder, and Procter. (*v.* Bull. 13, Chem. Div. of U. S. Dept. of Agric. 890).

A simpler method, giving good results, is that of Tatlock and Thomson, based on the precipitation of the tannin with quinine and weighing as quinine tannate. Cinchonine might be used with advantage instead of quinine as in Chapman's method for the estimation of tannin in hops (*v.* Analyst, 1910, 104).

The recorded percentages of tannin vary greatly, mainly owing to the different methods of analysis employed. In normal teas the tannin should not be less than about 6 p.c., but may exceed 20 p.c. Wigner's analyses gave the following results in exceptionally astringent teas :—

	Tannin p.c.
Mayon Young Hyson tea .	39·0
Very choice Assam . .	33·0
India Young Hyson . .	39·0
Assam (from Dr. McNamara's garden)	27·7
Caper, mixed . . .	42·3

The amount of *ash* is fairly uniform in all teas, and varies from a little below 5 to rather more than 7 p.c. It is always rich in potash and phosphates, and manganese is such a constant constituent as to be almost characteristic. Zöller found the constituents to be as follows (Doc. du Lab. Municip. de Paris, 500) :—

	P.c.
Potash	39·22
Soda	0·65
Magnesia	6·47
Lime	4·24
Oxide of iron	4·38
Manganous oxide	1·03
Phosphoric acid	14·55
Sulphuric acid	trace
Chlorine	0·81
Silica	4·35
Carbonic acid	24·30

The following results were obtained in the Inland Revenue Laboratory (J. Bell) :—

—	Congou (low)	Congou (fine)	Hyson	Souchong	Moning	Assam	Gunpowder (fine)
Total ash on dry tea . .	6·10	6·94	6·46	5·99	8·29	6·49	6·67
Sand	3·08	8·51	2·17	1·51	13·37	3·72	5·66
Silica	6·35	9·27	5·93	3·77	9·47	2·51	6·52
Chlorine	1·06	1·07	1·12	1·01	0·99	0·97	1·11
Potassium, to satisfy chlorine .	1·16	1·17	1·23	1·11	1·09	1·07	1·22
Potash, K_2O	34·38	28·87	35·66	34·29	26·83	37·71	30·69
Soda, Na_2O	0·62	1·07	0·80	0·34	0·50	0·97	1·27
Ferrous oxide, FeO . .	2·82	0·84	1·12	1·68	2·23	0·57	1·43
Alumina, Al_2O_3 . . .	5·55	3·42	2·73	4·19	4·52	1·54	2·70
Manganese oxide, Mn_3O_4 .	1·68	1·37	1·93	1·59	1·49	2·11	1·92
Lime, CaO	8·82	8·74	9·54	8·98	9·04	8·58	8·19
Magnesia, MgO . . .	2·12	4·87	4·65	3·19	2·42	6·48	6·52
Phosphoric anhydride, P_2O_5 .	14·11	14·68	14·11	18·54	12·69	14·74	16·15
Sulphuric anhydride, SO_3 .	6·52	6·54	6·34	6·38	5·39	5·83	6·68
Carbonic anhydride, CO_2 .	11·73	9·58	12·67	13·42	9·97	13·20	9·94

A determination of the amount of ash alone may serve to detect the presence of leaves other than those of the tea plant, for these usually differ largely from tea leaves in the amount of their ash. The soluble ash in genuine tea is relatively high, usually exceeding half the amount of total ash, whilst foreign leaves likely to be used as an adulterant for tea generally contain a much smaller proportion of soluble ash than genuine tea. Paraguay tea, however, contains about the same amount of ash as true tea, but a larger proportion of soluble ash.

Almost the whole of the insoluble portion of the ash dissolves in hydrochloric acid; the insoluble residue is usually less than 1 p.c., any excess being due to sand or silicious matter.

The table, p. 430, gives the amount of ash in various teas dried at 100°, together with the proportion of ash soluble in water and insoluble in dilute mineral acids, and the alkalinity of the ash (Bell).

In tea leaves which have been infused in the ordinary way for domestic use, the amount of ash and other constituents shown in the next table were as follows :—

Description	Percentage of ash	Percentage of Ash			Alkalinity as K_2O
		Soluble in water	Soluble in dilute acids	Insoluble in acids	
Congou .	3·92	0·54	2·97	0·41	0·11
Moning .	4·53	0·85	2·73	0·95	0·28
Orange Pekoe	3·77	0·68	2·52	0·57	0·18
Hyson .	5·56	0·76	3·40	1·40	0·21
Souchong .	4·12	0·81	2·61	0·70	0·19
Average .	4·38	0·73	2·85	0·81	0·19

Description	Percentage of		Percentage of ash			Alkalinity as K_2O
	Moisture	Ash	Soluble in water	Soluble in dilute acids	Insoluble in acids, sand	
Shanghai Congou, common	9·07	7·63	3·23	3·02	1·38	1·40
„ „ „	9·22	5·95	3·55	2·12	0·28	1·55
„ „ fine	8·51	7·41	4·02	2·54	0·85	1·76
„ „ „	8·56	6·62	3·72	2·25	0·65	1·50
„ Moyune Young Hyson, common	7·49	7·49	3·83	2·75	0·91	1·70
„ „ „ „ fine .	6·90	7·47	3·82	2·52	1·13	1·61
„ „ Hyson, common .	7·29	6·46	3·18	2·43	0·85	1·51
„ „ „ „ . .	7·25	6·55	3·82	2·37	0·36	1·71
„ „ „ fine . .	8·65	6·85	3·58	2·29	0·98	1·53
Foochow Congou siftings . . .	8·51	6·87	3·60	2·81	0·46	1·50
„ „ common . . .	9·35	7·34	3·37	2·97	1·00	1·55
„ „ fine . . .	9·09	6·89	4·01	2·32	0·56	1·77
„ Scented Orange Pekoe common	7·55	7·17	3·56	2·86	0·75	1·69
„ „ „ „ fine .	7·70	6·72	3·99	2·27	0·46	1·60
„ Souchong, common . .	8·45	6·43	2·97	2·76	0·70	1·51
„ „ „ . .	9·34	6·18	3·77	2·09	0·32	1·60
„ „ finest . . .	9·36	5·85	3·61	1·95	0·29	1·71
„ Moning, common . . .	8·92	6·88	3·55	2·57	0·76	1·44
Canton Scented Caper, common . .	6·87	6·38	3·21	·2·49	0·68	1·50
„ „ „ fine . .	6·63	6·63	3·47	2·23	0·93	1·46
„ „ Orange Pekoe, common	7·02	6·63	3·72	2·33	0·58	1·67
„ „ „ „ fine .	7·73	7·09	4·10	2·46	0·53	1·92
„ Gunpowder	7·08	6·70	3·54	2·54	0·62	1·31
Indian, Kangra Valley Young Hyson .	7·36	6·12	3·44	2·25	0·43	1·55
„ Pekoe Souchong . . .	8·28	6·28	3·24	2·42	0·62	1·60
Himalaya Orange Pekoe . . .	7·84	7·62	3·45	2·83	1·34	1·63
Chittagong „ „	8·92	6·20	4·23	1·77	0·20	1·86
Assam Orange Pekoe	9·41	5·93	3·78	1·93	0·22	1·63
„ Pekoe Dust	9·57	6·77	3·55	2·69	0·53	1·71
„ „	9·35	6·14	3·70	2·15	0·29	1·67
Darjeeling	9·06	5·73	3·68	1·86	0·19	1·67
Chittagong Congou	9·68	5·66	3·53	1·87	0·26	1·91
Average . .	8·31	6·64	3·62	2·40	0·63	1·62

Very little was known about the *essential oil* of tea prior to the researches of Van Romburgh in 1896, the chief results of which were as follows:—

440 lbs. of fresh leaves of tea distilled with water gave but *traces* of an essential oil, having a strong odour of tea. The water contained methyl alcohol and a very volatile product giving aldehyde reactions (possibly it contains diacetyl).

From *rolled and fermented* fresh leaves, besides the products above mentioned, an essential oil was obtained in larger amount (3 c.c. from 100 lbs. of tea), or about 0·006 p.c.

The oil has a yellowish colour and a penetrating odour of tea; sp.gr. 0·866 at 26°. It rotates polarised light 0° 10′ to the left in a 200 mm. tube. Fractional distillation separated it into two parts, the main portion boiling below 170° and the other above that temperature. The larger fraction consisted of a colourless liquid boiling from 153°–154° (bar. 740 mm.) with a strong odour of tea; sp.gr. 0·855 at 27°. Elementary analysis and the vapour density determinations indicated the formula $C_6H_{12}O$.

Sodium hydroxide and hydroxylamine have no action. With hydrochloric acid and acetic anhydride and with benzoylchloride and sodium hydroxide it gives esters. A solution of bromine in chloroform is decolorised with evolution of heat. It combines with 1 mol. of bromine. Treated with a neutral solution of potassium permanganate it is oxidised. All these reactions make it clear that the main portion of the oil consists of an unsaturated alcohol of the formula $C_6H_{11}OH$.

The higher boiling portions of the oil contained about 1 p.c. of methyl salicylate (Van Romburgh, private communication).

A *non-drying oil*, somewhat resembling olive oil, is obtained from tea-seeds in China and Assam, the former yielding from 30–35 p.c. and the latter from 43–45 p.c. of oil. The first pressings are used as an edible oil, although somewhat objectionable owing to the presence of saponin which is present to the extent of 7 or 8 p.c. in the resulting oil cake. It is therefore unsuitable for feeding purposes, but has been recommended for use as vermicide for dressing lawns. The lower qualities of oil are employed for illuminating, and for soap-making. Fine lubricating oils are also obtained from the seeds of other species of *Thea* in Japan.

The highest amount of *moisture* known in air-dried tea is 16 p.c. According to Wigner, the mean of the amounts yielded by driest Hysons and gunpowders and the moistest Congous is 7·67 p.c. Dragendorff found the average amount of moisture in twenty-three teas of Russian commerce to be 10 p.c. Péligot gives the amount in black tea as 10 p.c.; in green tea as 8 p.c. Bell (see table above) found in 32 samples of tea of different kinds and from various sources that the proportion of moisture varied from 6·6 to 9·7 p.c., the average being 8·3 p.c.

Nitrogen is present in tea both in the form of caffeine and albuminous bodies, and to a greater extent than in most other leaves. Choline and xanthine bases have also been identified in tea.

Péligot (Documents du Laboratoire Municipal de Paris, 501) gives the following percentages of total nitrogen:—

Gunpowder	6·62
Pekoe	6·28
Souchong	6·15
Assam	5·10

Gluten or *legumen* forms a quarter of the weight of the leaves according to Johnstone and Church (Chemistry of Common Life); but as it is hardly soluble in water, it is of no practical dietetic value. More will be dissolved if soda be added to the water. The 'brick tea' used in Thibet is boiled in the alkaline steppe-water which extracts the greater part of the gluten.

Tea infusion. The amount of matter extracted by water from tea is capable of giving useful indications, but truly comparable results can be obtained only by rigid uniformity in the details of the extraction process. The methods are based either on complete extraction and weighing either the extract or the insoluble portion, or partial extraction by infusion and determination of the specific gravity of the infusion.

Peligot (*vide supra*), using the first method, found the following percentages of *total extractive* on the dried leaves:—

Green teas.		*Black teas.*	
Gunpowder .	51·9	Assam . .	45·4
Hyson . .	47·7	Bohea . .	44·4
„ skins .	43·5	Congo . .	40·9
Young Hyson .	51·5	Pekoe . .	34·6
Imperial . .	43·1	„ orange .	48·7
Schoulang . .	45·9	Souchong (fine) .	45·7
Tonkay . .	42·2	„ (ordinary)	41·8

Tatlock and Thomson (Analyst, 1910, 104) adopted the second method, finding the extract by difference; and in order to avoid loss due to the solidifying out of extractive matter on cooling, they greatly increased the proportion of water, boiling 1 grm. of tea with 100 c.c. of water for 1 hour under a reflux condenser, filtering, washing with 80 c.c. of hot water, drying at 100°C. and weighing the insoluble residue on a tared filter. They found the following percentage of water extract:—

	Variations	Average
Indian teas (10) . . .	43·5–49·7	46·4
Ceylon „ (5) . . .	41·3–48·2	44·1
China „ (6) . . .	38·4–46·9	43·1

O. Kellner, in conjunction with S. Ishii and M. Kamoshita, determined the proportions of the constituents of tea in the *infusions ordinarily drunk* in Japan. The methods of making the infusions are, however, different from those employed in this country They are:

1. For Yencha, extra-fine green tea, the leaves are ground to powder, and drunk with the infusion.

2. For superior green tea the leaves are digested for 2 mins. with water at a temperature of 50°–60°C.

3. For medium green tea, boiling water is poured on the leaves, and stands on them for 1 minute.

4. For inferior tea, the leaves are boiled with water.

The object in all these methods is to get out as much caffeine and oil as possible, together with a moderate amount only of tannin.

Kellner digested 90 grms. superior green tea with half a litre of distilled water at 50°C. After 5 mins. the infusion was poured off, and another half-litre of water at 50°C. was added to the leaves. This was repeated three times, and each infusion was analysed separately.

The boiling-water method gives different results. Kellner digested 100 grms. of superior tea with 1 litre boiling distilled water, and the first infusion contained more than the sum of the contents of the three infusions by the warm-water method. The following table shows a summary of his results:—

PERCENTAGE AMOUNT OF EACH CONSTITUENT DISSOLVED.

	Warm water				
	First infusion	Second infusion	Third infusion	Total	Boiling water
Dry matter	5·3	4·7	3·6	13·6	16·1
Caffeine .	14·6	12·0	12·3	38·9	40·1
Tannin .	15·9	14·4	13·9	44·2	36·8
Total nitrogen	5·2	4·7	4·4	14·3	17·1
Ash . .	17·1	14·4	4·9	36·4	36·1
Potash .	15·1	15·1	6·1	36·3	43·3

In the following tables by Tatlock and Thomson (Analyst, 1910, 108) are shown the percentage of the total extractive, caffeine, and tannin obtained in a 3-mins. and a 5-mins. infusion respectively. The columns are numbered to correspond with the teas of which the proximate analyses are given above (p. 428).

RESULTS OF INFUSION PER 100 PARTS OF INGREDIENTS EXTRACTED.

——	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Three Minutes' Infusion.																						
Water extract	74	60	83	60	72	—	67	66	75	65	72	71	60	67	72	61	54	55	63	60	60	75
Caffeine .	76	55	59	39	73	—	46	50	73	51	69	60	41	67	69	72	66	54	73	73	68	68
Tannin .	61	46	70	41	57	—	58	56	57	50	52	60	42	58	59	49	39	41	46	41	49	42
Five Minutes' Infusion.																						
Water extract	88	73	90	70	83	—	79	79	83	72	89	85	76	85	89	75	65	67	71	78	77	81
Caffeine .	87	61	82	52	82	—	65	71	82	70	80	74	69	86	80	86	83	85	84	85	83	81
Tannin .	79	73	86	50	70	—	67	69	70	62	74	74	67	67	74	62	60	60	61	64	63	60

A strong decoction of tea frequently becomes turbid on cooling, and is covered with a thin pellicle caused by the separating out of caffeine tannate. The infusion also grows darker as it stands. This is probably due to the increase of tannin in solution and its alteration by oxidation.

With regard to infusions of tea, it should be remembered that different results are obtained from the same tea, according to whether the water used is hard or soft. The larger wholesale dealers have analyses made of the waters used in the different towns and districts which they supply, and blend different teas so as to suit the requirements of different neighbourhoods, the blend depending on the particular water used in each.

In judging the *commercial value* of tea the professional tea-taster makes an infusion by pouring about 100 c.c. of boiling water upon 3 grms. of tea, allowing to infuse for 5 mins. and then decanting the liquor. He is guided mainly by the colour, uniformity, and age of the leaf, and by the bouquet, flavour, and pungency of the infusion. These are usually supposed to depend upon the amount and quality of the volatile oil, but there is good reason to believe that they are intimately associated with the action of certain enzymes in the leaf.

Although considerations other than chemical composition affect the commercial value of tea, as the age, size, and condition of the leaf, whether whole, broken, tea dust, or fannings, yet in teas accepted by expert tea-tasters as of fine quality, a certain uniformity has been observed in the ratio of the caffeine to the tannin. This is as one to three, indicating a *compound* of caffeine and tannin already referred to as caffeine tannate (*see* Lancet, Jan. 1911).

In this form the special characteristics of both caffeine and tannin in the free state are neutralised in the compound, which differs in chemical and physiological properties from, and has none of the objectionable qualities of either of its constituents. In inferior or common teas either caffeine or tannin is present in excess of this ratio, the former imparting a bitter taste to the infusion, and the latter increasing its astringency. The proper balance may be attained by suitable blending.

Adulteration in its old forms is very little practised now, probably not at all in this country. Inferior teas from old stocks are sometimes sold, also teas recovered from wrecked vessels and re-dried, but owing to the examination by the Customs Authorities (acting under the Sale of Food and Drugs Act, 1875) of all tea imported into the United Kingdom, and the general soundness of the tea trade, the importation of adulterated tea is practically a thing of the past.

The modes of adulteration formerly common were :—

1. Adding leaves of different kinds, the principal being ash, beech, birch, bramble, camellia, chestnut, coffee, currant, elder, elm, gooseberry, hawthorn, plum, poplar, raspberry, and willow.
2. Adding 'exhausted' leaves, *i.e.* tea leaves that had already been used.
3. 'Facing' black tea with graphite and adding colouring matters to green tea, notably indigo, Prussian blue, turmeric, mixed with China clay, soapstone, &c. Copper salts are scarcely ever employed, but occasionally a little iron sulphate is used to impart astringency to the tea. The facing material rarely amounts to 1 p.c., and is usually free from deleterious ingredients, being for the most part insoluble in water.
4. Adding catechu and other astringent principles.
5. Adding sand containing ferric oxide to increase the weight of the tea.

Foreign leaves are detected by the microscope. Drawings of leaves principally used as tea adulterants will be found in Bell's Foods, in Bulletin No. 13, U.S. Dept. of Agriculture, and in Villiers and Collin's Traité des Altérations et Falsifications des Substances Alimentaires.

Indications as to the presence of exhausted leaves may be obtained by determinations of the caffeine, tannin, and in particular by the alkalinity of the ash and the proportion of it soluble in water.

The substances used for facing tea can generally be readily removed for examination by shaking up with cold water, pouring off the liquor, and allowing the matter in suspension to subside.

An imitation tea known as 'lie tea' was formerly made in China from the sweepings of the tea-warehouses, foreign leaves, and mineral matter, coloured by one of the facing preparations, cemented together by rice starch and rolled into grains. The percentage of ash in 'lie tea' was always high, often exceeding 50 p.c.

Brick tea. This variety of tea is used largely in Thibet, Western Siberia, and Russia. The cheaper and inferior kinds are very coarse, consisting of both leaves and twigs, frequently mixed with a glutinous rice paste to make them cohere, and compressed by hand into blocks. The curing of the leaf consists simply of a few minutes' heating in iron pans, a slight fermentation by storing in heaps in the 'hongs' or factories, then drying in the sun, sorting into grades, and steaming preparatory to pressure in shallow moulds of the required shape and size in which the blocks are left for 3 or 4 days to harden. Over twenty million pounds of this kind of tea are said to be consumed annually in Thibet.

A superior kind of brick tea is made, chiefly at Hankow, from tea dust which, after sifting and grading, is steamed and compressed in moulds into bricks or cakes by means of an hydraulic press, the blocks being left in the moulds for 2 or 3 weeks until thoroughly dry and hard.

Nearly fifty million pounds of this tea are made annually, chiefly for the Russian Government, in factories under Russian control, and large quantities of Indian tea dust are utilised in the manufacture of this variety of brick tea. The finest grades are made in 'tablet' form, mainly for consumption in European Russia.

Amongst certain Himalayan tribes in Thibet, and in Western Siberia, it is a common practice to *eat* the tea residue, after the infusion has been drunk, mixed with sugar, milk, butter, or other fat. It is very nutritious and forms the food of the natives for weeks at a time.

Different plants are used as tea in different parts of the world. The chief of these is the *Ilex paraguayensis*, or Brazilian holly, the leaves of which make what is known as Paraguay tea or 'maté' (*q.v.*).

Other plants whose leaves are used to make tea are:—

Angræcum fragrans (Thou.) (an orchid) makes the 'Faham tea' of Mauritius.

Catha edulis (Forsk.) makes 'Abyssinian tea,' known as 'Kât' or 'Kaat.'

Coffee-tree (*Coffea arabica* [Linn.]).

Cyclopia subternata (Vog.) ('Boer Tea,' 'Cape tea,' or 'Bush tea').

Glaphyria nitida (Jack) (a species of myrtle), in the Eastern Archipelago.

Ledum palustre (Linn.) and *Ledum latifolium* (Jacq.) make 'Labrador tea.'

Lithospermum officinale (Linn.) ('Gromwell') or 'Bohemian tea.'

Various species of *Melaleuca* and *Leptospermum* (belonging to the myrtle order), various species of *Correa* (belonging to the *Rutaceæ*); *Acæna Sanguisorbae* (Vahl.) (allied to the *Rosaceæ*), and the *bark* of the Australian *Sassafras*, make the 'Abyssinian tea' of Australia and Tasmania.

All the above teas, except Bohemian tea, Bush tea, and Faham tea, contain caffeine, and all have a volatile oil, and an astringent principle allied to tannin. J. C.

TELÆSCIN *v.* HORSE-CHESTNUT.

TELLURITE *v.* TELLURIUM.

TELLURIUM. Sym. Te. At.wt. 127·5; molec.wt. 255·0.

The presence of a new metal was suspected in an auriferous mineral from Transylvania by Müller von Reichenstein in 1782; from this mineral tellurium was isolated by Klaproth (Crell's Ann. 1798, 91). The element was more fully studied by Berzelius (Pogg. Ann. 1826, 8, 411; 1833, 28, 392; 1834, 32, 1, 577).

For researches on tellurium of a general character, *v.* Brauner (Monatsh. 1889, 10, 416), Staudenmaür (Zeitsch. anorg. Chem. 1895, 10, 189), Retgers (*ibid.* 1896, 12, 98), Gutbier (*ibid.* 1902, 32, 51, 54), Metzner (Ann. Chim. Phys. 1898, [vii.] 15, 203).

Occurrence.—Tellurium occurs native in small quantity, associated with silver and gold; but it is usually found combined with metals as tellurides, the most important being *tetradymite* (Bi_2Te_3), *altäite* (PbTe), *coloradolite* (HgTe), *calaverite* ($AuTe_2$), *sylvanite* ($AuAgTe_4$), *petzite* (Ag_3AuTe_2), *nagyagite* ($((AuPb)_2\,(TeSSb)_3)$). The chief localities are *Transylvania* (Petz, Pogg. Ann. 1842, 57, 467; Schönbein, Annalen, 1852, 86, 201; Loczka, Zeitsch. Kryst. 1892, 20, 317, 320; Muthmann and Schröder, *ibid.* 1897, 29, 140); *Colorado* (*v.* Chem. Soc. Abstr. 1896, 70, ii. 612, 613; 1898, 74, ii. 385; Amer. J. Sci. 1897, [iv.] 4, 306; 1898, [iv.] 5, 375, 377, 421, 428; 1900, [iv.] 10, 419, 427; 1904, [iv.] 18, 433; Bull. U.S. Geol. Survey, 1905, No. 262, 55); *West Australia* (*v.* Chem. Soc. Abstr. 1898, 74, ii. 385; Chem. News. 1900, 82, 272; Min. Mag. 1903, 13, 268; Eng. & Min. J. 1903, 75, 814; Ann. Mines, 1901, 19, 530); also *Mexico, Chile, Brazil, Honduras*, and *Asia Minor* (*v.* Bull. Soc. chim. 1873, 20, 481; Bull. Acad. roy. Belg. 1908, 255).

Tellurite (TeO_2) or *tellurium ochre* also occurs, and 17 p.c. of tellurium has been found in the *red sulphur* of Japan (Divers and Shimidzu, Chem. News. 1883, 48, 284).

Preparation.—Tellurium is obtained from the preceding minerals or from the residues obtained in several metallurgical processes. Bismuth telluride, finely powdered, is mixed with sodium carbonate, rubbed up with oil to a thick paste, and calcined in a closed crucible. After lixiviating with cold water, a current of air is drawn through the aqueous solution of sodium telluride, when tellurium separates as a grey powder. Other tellurides are attacked with hydrochloric acid, the insoluble residue heated with concentrated sulphuric acid, and from the diluted sulphate solution, after removing silver as the chloride, the tellurium is precipitated by means of zinc or sulphur dioxide. For details and other methods, *v.* Berzelius, *l.c.*; Löwe, J. pr. Chem. 1853, 60, 163; Oppenheim, *ibid.* 1860, 81, 308; Farbaky, Zeitsch. angew. Chem. 1897, 10, 11.

The alkaline residues from bismuth ores are acidified with hydrochloric acid and treated with sodium sulphide in order to precipitate the tellurium (Matthey, Proc. Roy. Soc. 1901, 68, 161). Tellurium is also extracted from the anode slimes obtained in the course of refining American copper by electrolysis (Whitehead, J. Amer. Chem. Soc. 1895, 17, 849, 855; Lenher, *ibid.* 1899, 21, 347, 351).

Crude tellurium may be purified by boiling it with sodium sulphide solution and sulphur; from the filtered liquid pure tellurium is precipitated by heating with sodium sulphite (Schelle, 7th Inter. Cong. Appl. Chem. 1909, sect. III. A. 80). For its complete purification, the element is dissolved in *aqua regia*, evaporated several times with hydrochloric acid, and precipitated by sulphur dioxide from the diluted and filtered chloride solution. The precipitate is fused with potassium cyanide in a current of coal gas, the mass extracted with water, filtered, and the tellurium precipitated by aspirating air through the solution. The element is converted into telluric acid by Staudenmaier's method (*v. infra*), purified by several recrystallisations, ignited to tellurium dioxide, and the latter dissolved in hydrochloric acid. The pure element, precipitated by sulphur dioxide or hydrazine from the chloride solution, is dried and distilled in a current of hydrogen (Brauner, Monatsh. 1889, 10, 416; Chem. Soc. Trans. 1889, 55, 382; Baker and Bennett, *ibid.* 1907, 91, 1849).

Properties.—Tellurium is a silver-white, lustrous, brittle, metallic-looking substance, of sp.gr. 6·27, which crystallises in hexagonal rhombohedra isomorphous with sulphur and selenium (Muthmann, Zeitsch. physikal. Chem. 1891, 8, 396). It melts at 452°, boils at a red heat, and volatilises readily when heated in a stream of hydrogen. In an almost perfect vacuum it boils at 478° (Krafft, Ber. 1903, 36, 4344). The vapour of tellurium is golden yellow, and consists of diatomic molecules (Deville and Troost, Compt. rend. 1863, 56, 891; Biltz, Zeitsch. physikal. Chem. 1894, 19 415).

Tellurium is precipitated by reducing agents in an amorphous form, sp.gr. 6·015. When heated, it is converted into the crystalline form with evolution of heat (Fabre and Berthelot, Compt. rend. 104, 1405; for a summary of literature on allotropy of tellurium, *v.* Cohen and Kroner, Chem. Weekblad. 1910, 7, 57).

By careful reduction in dilute solution, brown and blue colloidal solutions of tellurium can be prepared (Gutbier, Zeitsch. anorg. Chem. 1902, 32, 51, 91; 1904, 40, 264; 42, 177; Paal and Koch, Ber. 1905, 38, 534; Weimarn and Maljisheff, J. Russ. Phys. Chem. Soc. 1910, 42, 484).

For the emission spectrum of tellurium, *v.* Salet, Compt. rend. 1871, 73, 559, 742; Ann. Chim. Phys. 1873, 28, 49; Ditte, Compt. rend. 1871, 73, 262; Hartley, Chem. Soc. Trans. 1883, 43, 399; de Grammont, Compt. rend. 1898, 127, 866, 868; for spark spectrum, *v.* Watts, Spectrum Analysis, p. 28; and for absorption spectrum, *v.* Gernez, Compt. rend. 1872, 74, 1190.

Tellurium burns in air with a blue flame, forming the dioxide. It is not attacked by hydrochloric acid, but reacts with nitric or sulphuric acid, and also with concentrated potassium hydroxide. It is insoluble in carbon disulphide. Tellurium reduces solutions of gold and silver salts (Hall and Lenher, J. Amer. Chem. Soc. 1902, 24, 918) and reacts with thionyl chloride and similar chlorides (Lenher and Hill, *ibid.* 1908, 30, 737; Horváth, Zeitsch. anorg. Chem. 1911, 70, 408; Prandtl and Borinski, *ibid.* 1909, 62, 237), the tetrachloride being usually obtained. For its behaviour as an electrode, *v.* Le Blanc, Zeitsch. Elektrochem. 1905, 11, 521, 813, 931; 1906, 12, 649. In physical properties tellurium resembles the metals, but chemically it is decidedly non-metallic. It forms one of the oxygen family of elements and closely resembles sulphur and selenium. This is shown by the fact that the three elements are isomorphous, and form mixed crystals when crystallising either from solution in a solvent or from the fused mixture (*v. infra*). The compounds $Te(C_6H_5)_2Br_2$ and $Se(C_6H_5)_2Br_2$ are isomorphous, as also are selenium and tellurium dimethylamine bromides and chlorides; whilst the acid selenates and tellurates of rubidium have been shown to form mixed crystals (Muthmann, Zeitsch. physikal. Chem. 1891, 8, 396; Norris and Mummers, Amer. Chem. J. 1900, 23, 486; Pellini, Atti. R. Accad. Lincei, 1906, 15, i. 629, 711; 15, ii. 46; 1909, 18, i. 701; 18, ii. 19, 279).

Atomic weight. This is of particular interest, since, judging by the well-defined chemical similarities exhibited by sulphur, selenium, and tellurium, the atomic weight of tellurium would be expected to be less than that of iodine, in order that tellurium and iodine might fit into the Periodic Classification in the places that would be assigned to them from a consideration of their chemical properties. The atomic weight of tellurium is, however, found to be 127·5, distinctly higher than that of iodine (126·9). Numerous attempts to show that tellurium is not homogeneous (Brauner, Monatsh. 1889, 10, 411; Chem. Soc. Trans. 1889, 55, 382; Baker and Bennett, *ibid.* 1907, 91, 1849; Baker, Chem. News. 1908, 97, 209; Staudenmaier, Zeitsch. anorg. Chem. 1895, 10, 189; Pellini, Gazz. chim. ital. 1902, 32, 131; Gutbier, Sitzungsb. phys.-med. Soc. Erlangen, 1906, 37, 270; Norris. J. Amer. Chem. Soc. 1906, 28, 1675; Lenher, *ibid.* 1908, 30, 741; 1909, 31, 20; Marckwald. Ber. 1907, 40, 4730; 1910, 43, 1710) have failed; the positive results of Browning and Flint (Amer. J. Sci. 1909, 28, 347; 1910, 30. 209) have not been confirmed by Harcourt and Baker (Chem. Soc. Trans. 1911, 99, 1311; Dudley and Bowers, J. Amer. Chem. Soc. 1913, 875). The atomic weight has been determined on material prepared from widely different sources, by the syntheses and analyses of the dioxide and tetrabromide, by the analyses of telluric acid, the double bromide of tellurium and potassium, the basic nitrate, and other compounds, and by the measurement of its electro-chemical equivalent; the results point definitely to the value 127·5 as correct (*v.* the investigations cited above, and also Wills, Chem. Soc. Trans. 1879, 35, 704; Chikashigé, *ibid.* 1896, 69, 881; Gooch and Howland, Amer. J. Sci. 1894, 58, 375; Metzner, Compt. rend. 1898, 126, 1716; Koethner, Annalen, 1901, 319, 1; Scott, Chem. Soc. Proc. 1902, 18, 112; Gallo, Atti. R. Accad. Lincei. 1905, [v.] 14, i. 23, 104). The lower value obtained by Steiner (Ber. 1901, 34, 570) by the combustion of tellurium diphenyl has not been confirmed; and it still remains to be discovered why the positions of tellurium and iodine in the Periodic Classification, determined by their atomic weights, should be the reverse of those which their chemical properties indicate.

Tellurides. A number of these compounds occur as minerals (*v. supra*). The following have been shown to exist by the methods of thermal and microscopic analysis, the mercury compound alone having no melting-point: $AuTe_2$, Cu_4Te_3, Cu_2Te, HgTe, CdTe, Tl_2Te, Tl_5Te_3, Tl_2Te_5 PbTe, SnTe, Sb_2Te_3, As_2Te_3, Bi_2Te_3 (Pélabon, Compt. rend. 1906, 142, 207; 1907, 145, 118; 1909, 148, 1176; Fay and Ashley, Amer. Chem. J. 1902, 27, 95; Fay and Gillson, *ibid.* 27, 81; Fay, J. Amer. Chem. Soc. 1907, 29, 1265; Pellini and Aureggi. Atti. R. Accad. Lincei, 1909, 18, ii. 211; Pellini and Quercigh, *ibid.* 1910, 19, ii. 445; Chikashigé, Zeitsch. anorg. Chem. 1907, 54, 50; Biltz and Meklenburg, *ibid.* 1909, 64, 226; Kobayashi, *ibid.* 1910, 69, 1). By direct union of the elements K_2Te and Na_2Te can be obtained; numerous metallic tellurides have been prepared from aqueous solutions of these compounds by double decomposition; they are usually readily oxidised by air when moist (Tibbals, J. Amer. Chem. Soc. 1909, 31, 902). Carbon telluride CTe_2 is also known (Stock and Blumenthal, Ber. 1911, 44, 1832).

Hydrogen telluride TeH_2, discovered by Davy (1810), is formed by the direct union of its elements, or by the action of dilute acids on the tellurides of zinc, aluminium, and magnesium. It is prepared by electrolysing 50 p.c. sulphuric acid at −15°C., using a piece of tellurium as cathode; the gas evolved at the cathode, when quickly dried, is nearly pure hydrogen telluride. The substance is a fœtid-smelling, inflammable, extremely unstable gas, which condenses to a liquid boiling at 0°C. It has a vapour density of 65(H=1) and contains its own volume of hydrogen. It resembles hydrogen sulphide in chemical properties (Ernyei, Zeitsch. anorg. Chem. 1900, 25, 313).

COMPOUNDS WITH HALOGENS.

Tellurium tetrafluoride TeF_4 is formed when the dioxide is heated with hydrofluoric acid in a platinum retort; it distils over and forms a colourless, very deliquescent mass. The hydrate $TeF_4,4H_2O$ separates from solutions in hydrofluoric acid. Numerous double fluorides, *e.g.* $KF \cdot TeF_4$, $BaF_2 \cdot 2TeF_4,H_2O$ are known (Metzner, Compt. rend. 1897, 125, 23; Hogborn, Bull. Soc. chim. 1881, 35, 61; Wells and Willis, Amer. J. Sci. 1901, 12, 190).

Tellurium hexafluoride TeF_6, formed by the direct union of its elements, is a gas, slowly decomposed by water. Its molecular weight, determined from its vapour density, is 239, corresponding to the simple formula (Prideaux, Chem. Soc. Trans. 1906, 89, 320; *cf.* Moissan, Ann. Chim. Phys. 1891, [vi.] 24, 239).

Tellurium dichloride $TeCl_2$, formed by the direct union of its elements, is an almost black substance, which melts at 175°, and boils at 327°, yielding a deep red vapour having the normal density (Michaelis, Ber. 1887, 20, 2488, 2491); for the absorption spectrum of the vapour, *v.* Friederichs, Chem. Zentr. 1905, ii. 1073. The dichloride is decomposed by water into tellurium, tellurous and hydrochloric acids.

Tellurium tetrachloride $TeCl_4$ is formed when excess of either chlorine or sulphur chloride (Lenher, J. Amer. Chem. Soc. 1902, 24, 188) acts on tellurium. It is a white crystalline substance, which melts at 224° to a yellow liquid, and boils at 380°, giving a red vapour of normal density (Michaelis, *l.c.*). It is very hygroscopic, and is readily hydrolysed by water to tellurous and hydrochloric acids. It forms a large number of additive compounds with metallic chlorides, and also unites with hydrochloric acid (Wheeler, Amer. J. Sci. 1893, [iii.] 45, 267; Weber, Pogg. Ann. 1858, 104, 422; Metzner, Compt. rend. 1897, 125, 23; *cf.* Lenher and Titus, J. Amer. Chem. Soc. 1903, 25, 730; Lenher, *ibid.* 1900, 22, 136).

Tellurium dibromide $TeBr_2$, obtained by heating the tetrabromide with tellurium, is a black crystalline substance, melting at 280°, and boiling at 339°; the vapour is violet. It resembles the corresponding chloride (Brauner, Chem. Soc. Trans. 1889, 55, 410).

Tellurium tetrabromide $TeBr_4$, formed by the direct union of the two elements, can be sublimed *in vacuô*. It forms fiery red crystalline crusts when hot, orange yellow when cold; the density is 4·31. It melts at about 380°, and boils at about 420°, but the vapour undergoes dissociation into the dibromide and bromine. Tellurium tetrabromide dissolves in a small quantity of water, but is readily hydrolysed by an excess. It forms numerous double bromides, *e.g.* K_2TeBr_6 which crystallise beautifully and are easy to prepare (Wills, Chem. Soc. Trans. 1879, 35, 711; Wheeler, Amer. J. Sci. 1893, iii. 45, 267).

Tellurium diiodide TeI_2 does not appear to exist, the substance described by Berzelius being a mixture (Gutbier and Flury, Zeitsch. anorg. Chem. 1902, 32, 108).

Tellurium tetraiodide TeI_4, obtained by the action of hydriodic acid on tellurous acid (*cf.* Gooch and Morgan, Amer. J. Sci. 1896, 2, 271), is an iron-grey crystalline substance, which when heated melts and then decomposes. It forms double salts with metallic iodides (Wheeler, *l.c.*).

Tellurium dicyanide $Te(CN)_2$ can be obtained by the interaction of the tetrabromide with silver cyanide in benzene solution (Cocksedge, Chem. Soc. Trans. 1908, 93, 2176). It is decomposed by water.

OXIDES AND OXYACIDS OF TELLURIUM.

Tellurium monoxide TeO is a black powder, obtained by heating $TeSO_3$ to 230° *in vacuô* (Divers and Shimosé, Chem. Soc. Trans. 1883, 43, 319). It dissolves in concentrated sulphuric acid, forming a red solution from which *tellurium sulphate* is said to separate.

Tellurium dioxide TeO_2 is formed by burning tellurium in air, or by igniting tellurous or telluric acid, and is prepared by oxidising tellurium with warm nitric acid of sp.gr. 1·25 (Klein and Morel, Bull. Soc. chim. 1885, [ii.] 43, 198). It is a white, crystalline, dimorphous solid, which melts at a red heat and may be slowly sublimed. It is easily reduced to tellurium by hydrogen or carbon. It is practically insoluble in water, but dissolves in alkali hydroxides forming tellurites. The oxide is slightly basic, since it forms a basic sulphate $2TeO_2 \cdot SO_3$ and a basic nitrate $2TeO_2 \cdot HNO_3$ (Klein, Compt. rend. 1884, 99, 326; Ann. Chim. Phys. 1887, 10, 108; Norris, Fay and Edgerly, Amer. Chem. J. 1900, 23, 105).

Tellurous acid H_2TeO_3 is a light white powder obtained by pouring a solution of tellurium in dilute nitric acid into an excess of water, washing the precipitate and drying it over sulphuric acid. It is slightly soluble in water, and behaves as a weak, dibasic acid; the alkali salts only are soluble in water (Berzelius, Pogg. Ann. 1834, 32, 577; Oppenheim, J. pr. Chem. 1857, 71, 267).

Tellurous acid may be oxidised to telluric acid in either acid or alkaline solution; these reactions are used in its volumetric estimation (Brauner, Chem. Soc. Trans. 1890, 59, 238). It is reduced to tellurium by sulphur dioxide and other reducing agents.

Tellurium trioxide TeO_3 is an orange-yellow, crystalline mass of sp.gr. 5·07, obtained by heating telluric acid nearly to redness, and dissolving out any admixed dioxide from the residue by cold hydrochloric acid. It is insoluble in water, dissolves in concentrated potassium hydroxide, and slowly reacts with concentrated hydrochloric acid, being reduced to tellurous acid.

Telluric acid H_2TeO_4 may be obtained by decomposing its barium salt with sulphuric acid. It is best prepared by dissolving tellurium in nitric acid and boiling the strongly acid solution with chromic acid; on cooling the solution the dihydrate $H_2TeO_4,2H_2O$ crystallises out (Staudenmaier, Zeitsch. anorg. Chem. 1895, 10, 189). This hydrate is dimorphous, crystallising in both the monoclinic and the cubic systems (Gossner, Zeitsch. Kryst. 1904, 38, 498); its density is 3·05. The anhydrous acid is obtained by gently heating the dihydrate.

Telluric acid dihydrate dissolves in cold water very slightly, but is easily soluble in hot water. Sulphur dioxide and other reducing agents easily reduce it to tellurium. It behaves as a very feeble acid.

Another modification of the acid, allo*telluric acid*, is obtained by heating the dihydrate to

160° for some time; it dissolves very slowly in cold water and is a much stronger acid than the ordinary form (Mylius, Ber. 1901, 34, 2208; *cf.* Brauner, Chem. Soc. Trans. 1895, 67, 549; Gutbier, Zeitsch. anorg. Chem. 1902, 32, 96).

The alkali tellurates are soluble in water; those of the other metals are difficultly soluble in water, but readily soluble in hydrochloric acid (Gutbier and Wagenknecht, *ibid.* 1904, 40, 260; Hutchins, J. Amer. Chem. Soc. 1905, 27, 1157). Besides normal and acid tellurates, more complex salts, *e.g.*

$K_2TeO_4{\cdot}TeO_3,4H_2O$; $K_2TeO_4{\cdot}3TeO_3,4H_2O$ and $K_4TeO_5,8H_2O$ are known. A number of tellurates exist in two forms, one being white and soluble in water or acids, and the other being yellow and insoluble in these liquids (Berzelius). Complex compounds of telluric acid with iodates, phosphates, &c., are known (Weinland and Prause, Ber. 1890, 23, 1015; Zeitsch. anorg. Chem. 1899, 21, 43; 1901, 28, 45).

The molecular weight of telluric acid in aqueous solution corresponds to the formula $H_2TeO_4,2H_2O$, and it is therefore regarded as having the constitution $Te(OH)_6$.

Tellurates are reduced to tellurites either by ignition or by boiling with concentrated hydrochloric acid.

Tellurium sulphoxide $TeSO_3$, obtained by dissolving tellurium in pure sulphur trioxide, is a red amorphous solid, melting at 30°, which is decomposed by water (Weber, J. pr. Chem. 1882, [ii.] 25, 218; Divers and Shimosé, *l.c.*).

Tellurium sulphides. The precipitates obtained by passing hydrogen sulphide into solutions of tellurites and tellurates, and which were described by Berzelius as sulphides, are simply mixtures of sulphur and tellurium (Becker, Annalen, 1876, 180, 257; Brauner, Chem. Soc. Trans. 1895, 67, 545; Gutbier and Flury, Zeitsch. anorg. Chem. 1902, 32, 272). The substance initially precipitated from a cold solution of a tellurite appears to be a mixture of TeS and S, the former decomposing on standing (Snelling, J. Amer. Chem. Soc. 1912, 34, 802). No compound has been isolated from fused mixtures of the two elements, which form two series of mixed crystals, and are therefore isodimorphous (Pellini, Atti R. Accad. Lincei, 1909, [v.] 18, i. 701; ii. 19; Jaeger, Proc. K. Akad. Wetensch. Amst. 1910, 12, 602; Chikashigé, Zeitsch. anorg. Chem. 1911, 72, 109). The sulphides appear to exist, however, in colloidal solution (Gutbier, Zeitsch. anorg. Chem. 1902, 32, 272, 292) and thiotellurites and thiotellurates have been isolated (Berzelius, Pogg. Ann. 1826, 8, 411; Oppenheim, J. pr. Chem. 1857, 71, 267).

Organic Derivatives.

Diethyl telluride $Te(C_2H_5)_2$ *v.* Ethyl.

Dimethyl telluride $Te(CH_3)_2$, obtained from methyl barium sulphate and potassium telluride, is a pale-yellow oil, with a garlic odour. The diiodide is obtained by heating tellurium with methyl iodide; and from this *trimethyl tellurium iodide* $Te(CH_3)_3I$ is prepared by the action of methyl iodide, sodium sulphite, and sodium carbonate (Wöhler and Dean, Annalen, 1855, 93, 233; Heeren, *l.c.*; Demarçay, Bull. Soc. chim. 1883, [ii.] 40, 100; Scott, Chem. Soc. Proc. 1904, 20, 157).

Diphenyl telluride $(C_6H_5)_2Te$ is obtained by heating mercury diphenyl with tellurium (in CO_2). It is a liquid, boiling at 312°–320°. The *dibromide* forms small yellow prisms, melting at 203·5°; it is converted into the *oxide* by warming with sodium hydroxide (Krafft and Lyons, Ber. 1894, 27, 1769; Pellini and Menin, Gazz. chim. ital. 1900, 30, ii. 472).

Di-α-naphthyl telluride $Te(C_{10}H_7)_2$ melts at 126·5°; the dichloride and dibromide of this compound melt at 265° and 244° respectively (Lyons and Bush, J. Amer. Chem. Soc. 1908, 30, 831).

For the *chloride, bromide,* and *iodide* of *tellurium triphenyl,* and their derivatives, *v.* Lederer, Compt. rend. 1910, 151, 611; *see* also Rust, Ber. 1897, 30, 2828; Rohrbaech, Annalen, 1901, 315, 9.

Detection and estimation of tellurium.—Tellurium is precipitated (by reducing agents or by electrolysis) as the element and weighed as such, or else precipitated and weighed as dioxide; numerous volumetric methods have been devised, *v.* Analysis, and Divers and Shimosé, Chem. Soc. Trans. 1883, 43, 329; McIvor, Chem. News, 1902, 86, 308; 1903, 87, 17; Gutbier, Zeitsch. anorg. Chem. 1904, 41, 448; 1902, 32, 260, 295; Pellini, Atti. R. Accad. Lincei, 1903 12, ii. 312; 1904, 13, ii. 275; Gallo, *ibid.* 1904, 13, i. 713; Pellini, Gazz. chim. ital. 1903, 33, i. 515; Brauner and Kuzma, Ber. 1907, 40, 3362; Lenher and Homberger, J. Amer. Chem. Soc. 1908, 30, 387; Perkins, Amer. J. Sci. 1910, 29, 540.

TELLURIUM OCHRE *v.* Tellurium.

TEMPER. An alloy of arsenic and lead sometimes used for hardening shot, *v.* Arsenic, alloys of; also, Tin.

TEMPER-CARBON is the name given to the carbon liberated during the tempering of steel. The change consists in the formation of a conglomerate of temper-carbon, ferrite and pearlite from a mixture of pearlite and cementite. It is identical with ordinary graphite (Charpy, Compt. rend. 1907, 145, 1173).

TENNANTITE *v.* Fahl-ore.

TERBIUM. Sym. Tb. At.wt. 159·2. This extremely rare element is present as oxide in the terbia earths which form a connecting link between the more basic cerite earths and the less basic ytterbite earths. The crude 'terbia' consists mainly of gadolinia, but it owes its characteristic yellow colour to the presence of small quantities of terbium peroxide. The existence of this elusive element, terbium, was first indicated by Mosander in 1843, but more than 60 years elapsed before its oxide and salts were isolated in a highly purified condition.

Occurrence.—In small quantities in monazite, cerite, ytterbite (gadolinite), samarskite, äschynite, and other minerals containing the rare earths (*v.* Cerite earths).

Separation and purification. The most soluble portions of the double ammonium or magnesium nitrate fractionation (*v.* Neodymium) form a convenient starting-point for the separation of the three metals of the terbium group, namely, europium, gadolinium, and terbium. A preliminary separation of the cerite metals with potassium sulphate is not to be recommended, since appreciable amounts of the terbium metals are co-precipitated with the sparingly soluble double sulphates.

Methods of separation based on (1) fractional precipitation with ammonia, (2) fractional crystallisation of double sulphates, ethyl sulphates, oxalates or formates lead rather to a concentration of the terbium group than to a separation of its components, the chief constituent gadolinium being the only one isolated in a moderately pure state by any of these processes (*cf.* EUROPIUM and GADOLINIUM).

The separation of terbium from gadolinium was first accomplished by crystallising repeatedly the double nickel nitrates and then precipitating the bases fractionally with ammonia. In this way 7 grms. of pure terbia were obtained (Urbain, Compt. rend. 1904, 139, 736; 1905, 141, 521).

Fractionation of the double magnesium nitrates of the terbia-yttria group from monazite, followed by an application of the basic salt method (*v.* SCANDIUM), and final repeated crystallisation of the oxalates lead to a separation of terbium (Feit, Zeitsch. anorg. Chem. 1905, 43, 267).

The nitrates of gadolinium and terbium, unlike the other salts of these metals, differ somewhat widely in solubility. Bismuth nitrate, which is more soluble in nitric acid than gadolinium nitrate, and slightly less soluble than terbium nitrate, is added in excess to an acid solution of the two salts. A complete separation of gadolinium and terbium is effected by fractional crystallisation of the mixture. The terbia thus isolated is identical with the products obtained in the foregoing separations, and its metal is identical with the elements provisionally indicated by the symbols Z_δ, Z_β (Lecoq de Boisbaudran), Γ (Demarçay), and G_β (Crookes).

Terbium oxide (*terbia*) Tb_2O_3 is white and the terbium salts with colourless acid radicles are themselves colourless.

Terbium peroxide Tb_4O_7, dark-brown or black mass produced by igniting terbium oxalate or sulphate respectively; it dissolves in mineral acids to form the following salts which are neutral to litmus: **terbium nitrate**

$$Tb(NO_3)_3,6H_2O,$$

m.p. 89°, monoclinic crystals; **terbium sulphate** $Tb_2(SO_4)_3,8H_2O$, micaceous lamellæ; **terbium chloride** $TbCl_3,6H_2O$, very hygroscopic, transparent, prismatic crystals.

Spectra.—Absorption spectrum, 1 band (λ488) in blue, and 9 in ultra-violet (Compt. rend. 1904, 139, 1015). Spark spectrum, very complex (*ibid.* 1906, 142, 957; Sitzungsber, Akad. Berlin, 1906, 384)

Pure terbia gives no cathode luminescence, but traces of this oxide mixed with gadolinia and aluminia produce respectively a green and white luminescence, the latter effect being remarkably striking. G. T. M.

TEREBENE *v.* OILS, ESSENTIAL; and TERPENES.

TEREBIC ACID *v.* LACTONES.

TEREPHTHALIC ACID *v.* PHTHALIC ACID.

TERPENES. The name 'terpene' has been, until recently, applied to unsaturated hydrocarbons having the empirical formula $C_{10}H_{16}$, which exist widely diffused in the vegetable kingdom as constituents of various essential or volatile oils. Of these, essence, oil, or spirit of turpentine is one of the most characteristic and best known. Of late years the term has been extended somewhat so as to include such compounds as menthene $C_{10}H_{18}$, and certain homologues of the terpenes $C_{10}H_{16}$, produced by artificial synthetical processes.

The terpenes in nature are associated with products which have probably been formed from them, or simultaneously with them by polymerisation, oxidation, or the action of water and acids. These products are often of greater importance as perfumes or medicinal agents than the terpenes with which they are diluted, as, for example, in such cases as the essential oils of lemon, bergamot and other fruits of the natural order *Aurantiaceæ*, the essences extracted from the mints and other plants of the *Labiatæ*, those of caraway and other fruits of the *Umbelliferæ*. On the other hand, the varieties of spirit of turpentine obtained from the wood, leaves, or fruits of various *Coniferæ* are of great practical importance as solvents, and in the production of paints and varnishes (*v.* OILS, ESSENTIAL).

For the purposes of this article it will be convenient to restrict the name *terpene* to the hydrocarbons $C_{10}H_{16}$, except in a few cases specifically indicated. The name *hemiterpene* may be applied to compounds of half this molecular weight, C_5H_8; the name *sesquiterpene* to those of the formula $C_{15}H_{24}$, and the name *polyterpene* to the more complex polymerides $C_{20}H_{48}$, &c.

Compounds containing more than 16 atoms of hydrogen to 10 atoms of carbon may be called *hydroterpenes*.

The terpenes are generally liquids having a characteristic odour, not sensibly soluble in water, and of lower density than water, to which they communicate their peculiar taste and odour (Distilled Waters of Pharmacy). They are miscible to a large though limited extent with alcohol and miscible in all proportions with glacial acetic acid. The natural terpenes are all optically active, some being dextro- and others lævorotatory.

Spirit of turpentine has been known for ages as obtainable by distillation with water of the natural exudation from various pine and fir trees. One of the first recorded facts relating to the chemistry of the terpenes is the production of the solid hydrochloride by passing hydrogen chloride into turpentine oil (Kind, Tromsdorff's Journ. d. Pharmacie, xi. pt. ii. 132, 1803). This was for a long time confused with common camphor, and is still sometimes referred to as 'artificial camphor.'

It was not until Liebig's process for the analysis of organic compounds had been perfected that the composition of spirit of turpentine was known, and it was shown that essence of lemon has the same formula (Dumas, Annalen, 1833, 6, 245; also Blanchet a. Sell, and *ibid.* 262).

It was known that the terpene from essence of lemon boils at a temperature about 20° higher than the b.p. of spirit of turpentine, but down to about 1876 it was supposed that there was an indefinitely large number of hydrocarbons of same formula $C_{10}H_{16}$, and no classification had been attempted. Tilden and Shenstone then obtained the nitrosochlorides (Chem. Soc.

Trans. 1877), and from a study of these compounds Tilden divided the then known terpenes into three classes (Chem. Soc. Trans. 1878) as follows: (1) turpentines or terpenes proper, (2) citrenes or limonenes, (3) sylvestrene, discovered by Atterberg (Ber. 10, 1202). Disregarding for the present the polyterpenes, the following additional groups must now be recognised: terpinene, terpinolene, *iso*pinene, pinolene, phellandrene, fenchene, camphene, carvestrene, *iso*carvestrene, and other menthadienes, thujene, sabinene. *cyclo*-Pentanes C_9H_{14} and various open-chain hydrocarbons resembling *cyclo*-terpenes, as closely allied compounds, must also be taken into account. Since 1885 the terpenes and their derivatives have been studied by many chemists. The most important systematic researches are those of O. Wallach (Annalen, 225, &c.), A. von Baeyer (Ber. 26, &c.) and W. H. Perkin, junr. (Chem. Soc. Trans. 1904, &c.).

The several hydrocarbons will now be described under the names which have been, for the most part, introduced by Wallach.

Cyclic Terpenes.

1. **Pinene group** (=turpentines or terpenes proper).

Australene, or dextro-pinene, of which rectified American turpentine, from *Pinus palustris* (Mill.) and *P. Tæda* (Linn.), and especially the Burmese turpentine from *P. Khasya* (Griff.), almost wholly consists, is obtained by agitating the commercial oil with an alkaline solution, drying completely, and carefully fractionating (156°). Dextrorotatory $[\alpha]_D=+40\cdot5$. Sp.gr. 0·8765 at 0°/4°, 0·8586 at 25°/25°, 0·8278 at 100°/100° (Tilden, unpublished experiments). This compound is also a constituent of many volatile oils, *e.g.* Russian and Swedish turpentine oils, from *Pinus sylvestris* (Linn.), and *P. Ledebourii* (Endl.) (Tilden, Chem. Soc. Trans. 33, 80); wormwood and spearmint (Brühl, Ber. 21, 156), and many others.

Terebenthene or lævopinene. French turpentine oil, from *P. Pinaster* (Soland.), consists chiefly of this hydrocarbon. B.p. 156°. $[\alpha]_D=-40\cdot32$. Sp.gr. 0·8767 at 0°/0°, 0·8619 at 17·88°/17·88° (Riban, Compt. rend. 78, 788; 79, 314). Present also in oil of rosemary (Bruylants, J. 1879, 944), oil of lemon (Tilden, Pharm. J. [3] 9, 654), sage and juniper (Chem. Soc. Trans. 31, 554), thyme and anise (Brühl, Ber. 21, iii. 156), and others.

For production and properties of turpentine oils *v.* Oils, essential.

Both dextro- and lævo- rotatory pinenes from different sources differ considerably in rotatory power, owing to the presence in varying quantities of hydrocarbons of opposite rotatory power. Pure pinene, optically inactive (b.p. 155°–156°, sp.gr. 0·858 at 20°, ref. power $n_D=1\cdot46553$ at 21°), is obtained by the decomposition of the nitrosochloride by aniline (Wallach, Annalen, 258, 243), or better by methylaniline or dimethylaniline (Tilden, Chem. Soc. Trans. 1904, 763). All varieties of pinene agree in the following chemical characters.

Dry hydrogen chloride unites with the hydrocarbon, forming a monohydrochloride $C_{10}H_{16}HCl$, m.p. 125°. If the pinene used is not quite free from moisture a certain amount of dipentene dihydrochloride is formed, and this, with the monohydrochloride, forms a liquid from which the latter can be only partially recovered by fractional distillation or cooling. Pinene obtained by fractional distillation from ordinary turpentine oil contains small quantities of isomeric hydrocarbons (pinolene, β-pinene), which yield liquid hydrochlorides. From such pinene, therefore, the theoretical yield of monohydrochloride is never obtained.

The hydrochloride obtained from dextropinene is dextrorotatory, that from lævopinene is lævorotatory.

In the presence of water, alcohol, ether, or acetic acid, hydrogen chloride forms a dihydrochloride $C_{10}H_{16}2HCl$, m.p. 50° (*v. Dipentene, infra*).

Nitrosyl chloride gas passed into a solution of the terpene in chloroform at −10° forms a nitrosochloride $C_{10}H_{16}NOCl$ (Tilden, Chem. Soc. Trans. 1875, 514, and 1877, i. 554), the same compound being formed by the action of hydrochloric acid on a cooled mixture of the terpene with amyl or ethyl nitrite and glacial acetic acid (Wallach, Annalen, 245, 245). The best yield of nitrosochloride is obtained when a mixture of dextro- and lævo- pinenes is employed in proportion to provide an optically inactive liquid. When strongly active pinene, dextro- or lævo-, is used the product is small. This appears to be due to the fact that the nitrosochloride is bimolecular $[C_{10}H_{16}NOCl]_2$ (Baeyer, Ber. 1895, 28, 648), and is optically inactive by internal compensation, and when an active variety is used one half of the hydrocarbon or the nitrosochloride undergoes inversion, the change being attended by evolution of heat. The melting-point of the nitrosochloride is usually from 103° to 105°, but after careful recrystallisation from chloroform it is 115° (Tilden, Chem. Soc. Trans. 1904, 85, 759).

The nitrosochloride heated with alcoholic potash yields an *iso*nitroso compound $C_{10}H_{15}NO$, m.p. 132°. (For crystallography *see* Story-Maskelyne, Chem. Soc. Trans. 1875, 518; and Phil. Mag. 1879, 129.)

Primary and secondary fatty amines react with the nitrosochloride producing nitrolamines which possess characteristic properties. The nitrolbenzylamine $C_{10}H_{16}NO\cdot NH\cdot CH_2\cdot C_6H_5$ melts at 122°, and the piperidide

$$C_{10}H_{16}\cdot NO\cdot N : C_5H_{10}$$

melts at 118°–119° (Wallach). Alcoholic ammonia converts the nitrosochloride into the nitrolamine $C_{10}H_{16}NO\cdot NH_2$, m.p. 123°–125° (Leach, Chem. Soc. Trans. 1907, 91, 1).

Pinene nitrosochloride interacts in a different way with aniline and aromatic bases generally. Primary bases give a diazo compound, while secondary bases yield a nitroso- compound, the hydrocarbon being in both cases regenerated in an optically inactive form.

The nitrosochloride interacts with potassium cyanide in the presence of alcohol, yielding the monomolecular cyanide or nitrile

$$C_{10}H_{15}(N\cdot OH)CN$$

m.p. 71° (Tilden and Burrows, Chem. Soc. Trans. 1905, 87, 344).

Pinene nitrosochloride also interacts with sodium azide in the presence of alcohol, producing a pinenenitrosoazide $C_{10}H_{15}(N\cdot OH)N_3$ which melts at 120°. When this compound is boiled with water it is converted partly into an isomeride, melting at 126°, and partly into the oxime of hydroxydihydrocarvone (m.p. 133°·5) already described by Wallach (Forster and Newman, Chem. Soc. Trans. 1911, 99, 244).

Pinene appears to combine with four atoms of bromine, but the product is unstable and quickly evolves hydrogen bromide. If two atomic proportions of bromine are added to a mixture of pinene and carbon tetrachloride a dark liquid is obtained, from which a small quantity of a crystalline dibromide $C_{10}H_{16}Br_2$, m.p. 169°–170°, can be extracted. When heated with aniline this compound yields ordinary cymene (Wallach, Annalen, 264, 1).

Pinene, mixed with alcohol and nitric acid, yields crystallised terpin hydrate, a compound which has long been known as a product of the prolonged contact of turpentine with various aqueous liquids (Wiggers, Annalen, 33, 358; 57, 247; Tilden, Chem. Soc. Trans. 33, 247; Hempel, Annalen, 180, 71; *see* also *Terpineol, infra*).

When exposed to air or oxygen in the presence of sunlight pinene yields a crystalline compound $C_{10}H_{18}O_2$, discovered by Sobrero (Compt. rend. 33, 66). This is also readily formed by oxidising pinene by means of an aqueous solution of mercuric acetate (Henderson and Agnew, Chem. Soc. Trans. 1909, 95, 289). This compound, sometimes known as *sobrerol*, possesses the properties of a tertiary alcohol. When distilled with dilute acid it loses the elements of water, and yields a compound $C_{10}H_{16}O$, which is identical with one of the products of the action of nitrous acid on pinene, isolated by Wallach and Otto, and called by them *pinole* (Annalen, 253, 249). The alcohol is dextro- or lævo- rotatory according to the character of the terpene from which it is formed. The pure substance melts at 150°, but when equal weights of the two varieties are mixed an inactive compound is obtained, which melts at 131° (Armstrong and Pope, Chem. Soc. Trans. 59, 311). Pinole is an unsaturated compound and yields a crystalline dibromide, m.p. 94°, a hydrochloride and hydrobromide, and a nitrosochloride, m.p. 103°. From the last-named compound a series of nitrolamines have been obtained. By oxidation with permanganate pinole readily yields terpenylic acid $C_8H_{12}O_4$, together with small quantities of other products.

When pinene is oxidised by nitric acid two main products are obtained, namely terebic acid $C_7H_{10}O_4$ and terpenylic acid $C_8H_{12}O_4$. If permanganate is used the chief product is α-pinonic acid $C_{10}H_{16}O_3$ (Baeyer, Ber. 1896, 29, 3).

Pinene distilled with bleaching powder and water yields a large quantity of chloroform. Picric acid has no action on the pinenes at ordinary temperatures, but at the boiling-point of the hydrocarbon a brisk reaction sets in, and after cooling a pale yellow crystalline compound is deposited, which on boiling with alkali yields borneol (Lextreit, Compt. rend. 102, 555; Tilden and Forster, Chem. Soc. Trans. 1893, 63, 1388).

2. **β-Pinene** (tropinene) is supposed to occur in turpentine oil in small quantity. It has been obtained, together with fenchene, from nopinone, a ketone obtained by Baeyer among the products of oxidation of turpentine oil. Nopinone was prepared and further studied by Wallach and Blumann (Annalen, 1907, 356, 227; Wallach, 1908, 363, 1). The synthetical β-pinene unites with hydrogen chloride to form bornyl chloride [117°–120°] and dipentene dihydrochloride [49°–50°].

3. **Limonene group** (=citrenes).

Dextro-limonene, b.p. 175°–176°, sp.gr. 0·846 at 20°. When obtained from oil of orange $[\alpha]_D = +106°{\cdot}8$ *ca.* (Wallach, Annalen, 252, 145). This hydrocarbon constitutes the chief ingredient in oils of orange, bergamot, lemon, and limes; it is also present in oils of carraway, pine needles (*P. sylvestris* ?), dill, erigeron, &c.

Lævo-limonene is contained in the oil of Scotch fir leaves (*P. sylvestris* [Linn.]), sometimes called 'Firwool oil' (Tilden, Chem. Soc. Trans. 33, 83; Wallach, Annalen, 227, 287). A specimen, believed to have been obtained from leaves of *P. picea*, gave b.p. 175°–176°, sp.gr. 0·846 at 20°/20°, $\alpha]_D = -105°$ (Wallach, *ibid.* 246, 221).

The limonenes are distinguished by giving with hydrogen chloride a liquid monochloride, and a dihydrochloride, m.p. 50°, identical with that obtained from the pinenes; also a nitrosochloride $C_{10}H_{16}NOCl$, either by the direct addition of nitrosyl chloride (Tilden and Shenstone) or by action of amyl or ethyl nitrite and hydrochloric acid (Wallach). From the nitrosochloride is obtained a nitroso compound, m.p. 72°, which, when prepared from *lævo*-limonene, is identical in every respect with carvoxime $C_{10}H_{14}N{\cdot}OH$ from carvone. (For Crystallography *v.* N. Story-Maskelyne, Phil. Mag. 1879, 132; for a comparison of the rotatory powers of the two limonenes and their derivatives *v.* Wallach, Annalen, 252, 141). The limonenes are further characterised by the formation of a crystalline tetrabromide $C_{10}H_{16}Br_4$, m.p. 104°–105°, by direct addition of bromine (Wallach, *ibid.* 227, 277).

The nitrosochloride obtained as described above either from dextro- or lævo- limonene is always a mixture of two compounds, which are separable from each other by means of cold chloroform in which the α- compound is more soluble than the β-. The former crystallises from ether in large clear crystals, the latter in needles. There is a slight difference of melting-point, and the α- compound has in each case a greater rotatory power than the β-. α-Nitrosochloride, m.p. 103°–104°, $[\alpha]_D = +$ or $-314°$ (Conrady, Annalen, 252, 145). β-nitrosochloride, m.p 105°–106°, has $[\alpha]_D = +$ or $-241°$*ca.* Wallach has traced the characters of some of the nitrolamines derived from the two nitrosochlorides, and finds that those derived from the α- compound are identical with those from the β- compound (Annalen, 252, 113). The corresponding nitrosocyanides, however, do not appear to be the same, neither do the products formed by the action of magnesium methyl iodide on the α- and β-nitrosochlorides respectively (Tilden and Shepheard, Chem. Soc. Trans. 89, 920; also Tilden and Leach, *ibid.* 85, 931).

Dipentene (*limonene*) is the racemic compound formed by mixing together equal quantities of dextro- and lævo-limonenes. Just as racemic acid and its salts differ in some physical characters from tartaric acid and the tartrates, so dipentene differs in some respects from the limonenes. Although the boiling-point of the inactive mixture is nearly the same as that of the limonenes, such differences as the following are observed in the melting-points of derivatives:—

	Limonene	Dipentene
Tetrabromide $C_{10}H_{16}Br_4$.	105°	124°
d or *l*-Carvoxime $C_{10}H_{14}NOH$	72°	93°

&c. (Wallach, Ber. 1891, 24, 1559).

The name 'dipentene' includes diisoprene, *iso*terebenthene, formed by the action of heat on terebenthene, cinene, cajeputene, and also caoutchene, one of the products of the destructive distillation of caoutchouc (*q.v.*). Dipentene is produced, together with terpinene terpinolene, and terpineol by the action of sulphuric or phosphoric acid on terpin, or by the action of sulphuric acid on the pinenes under certain conditions. The product thus obtained was formerly called 'terpilene.' Dipentene may be prepared from the dihydrochloride, m.p. 50°, obtained from either limonene or moist pinene, by the action of heat on the chloride (Tilden, Ber. 12, 1133), or by boiling it with a mixture of sodium acetate and acetic acid, or with alcohol and aniline (Wallach). Dipentene thus obtained is, however, accompanied by considerable quantities of cymene, terpinene, terpinolene, together with a small amount of a saturated hydrocarbon of boiling-point 155° (Tilden, Chem. Soc. Trans. 1893). The foregoing methods are all artificial; among the natural products in which dipentene is known to exist are the volatile oils of the camphor tree (Wallach, Annalen, 227, 296), also oil of elemi, and in Russian and Swedish turpentine (Wallach), and many other essential oils.

When prepared from the dihydrochloride with the utmost care by the action of aniline, dipentene appears to be accompanied with another hydrocarbon, perhaps ψ-limonene, which raises the boiling-point to 177°–178° (Wallach, Ber. 1907, 40, 600).

Dipentene, like the limonenes, unites with only one molecule of hydrogen chloride when presented in the form of the dry gas; in the presence of moisture all unite with 2HCl to produce the optically inactive saturated compound $C_{10}H_{16}2HCl$, m.p. 50°, which is identical with the dihydrochloride, formed under the same circumstances from pinene.

Dipentene yields a nitrosochloride, m.p. 101°–102°, which, like the corresponding compounds from the limonenes and from pinene, is bimolecular. It yields an inactive carvoxime, m.p. 93°, which may be formed by mixing together equal weights of lævocarvoxime, m.p. 72°, from dextrolimonene and dextrocarvoxime, m.p. 72°, from lævolimonene. This compound, notwithstanding the difference of melting-point, gives by Raoult's method a molecular weight corresponding to the simple formula $C_{10}H_{15}NO$ (Wallach, Annalen, 246, 230).

When α- limonene nitrosochloride (*v. Limonene*), prepared from either dextro- or lævolimonene, is warmed with an alcoholic solution of piperidine, a mixture of two crystallisable nitrolamines results in each case, as follows:

Nitrolpiperidines $C_{10}H_{16}\cdot NO\cdot NC_5H_{10}$.

From lævolimonene.

α-compound, m.p. 93°–94°. Rhombic (from alcohol). $[\alpha]_D=-67\cdot60^\circ$. Hydrochloride *dextro*-rotatory.

β-compound, m.p. 110°–111°. Monosymmetric. $[\alpha]_D=+60\cdot18^\circ$. Hydrochloride almost inactive.

From dextrolimonene.

α-compound, m.p. 93°–94°. Rhombic. $[\alpha]_D=+67\cdot75^\circ$. Hydrochloride *lævo*- rotatory.

β-compound, m.p. 110°–111°. Monosymmetric. $[\alpha]_D=-60\cdot48^\circ$. Hydrochloride ?

Similar results have been obtained by the employment of aniline and benzylamine. The salts of the bases thus produced possess in every case a rotatory power opposite in direction to that of the base from which each is derived.

From the foregoing statement it is clear that from each of the two active modifications of limonene two distinct series of bases are derived. Two other series may be formed from the inactive hydrocarbon. Thus when the two α-piperidine bases, m.p. 93°–94°, above described are dissolved in petroleum spirit, and the solutions mixed, an inactive nitrolamine, m.p. 154°, is at once precipitated. A second inactive compound, m.p. 152°, is formed in like manner by mixing the β- limonene bases (Wallach, Annalen, 252, 123).

Limonene oxidised with a weak solution of permanganate gives first a tetrahydric alcohol $C_{10}H_{16}(OH)_4$, m.p. 191·5°–192°, which crystallises in needles and has a faintly sweet taste (G. Wagner, Ber. 23, 2307). By oxidation with nitric or chromic acids limonene yields terpenylic acid (Krafft and Sauer, *ibid.* 1877, 10, 522).

Pure dextrolimonene and lævolimonene give when oxidised no toluic or other benzenoid acid, and pure dipentene, which may be obtained from the products of destructive distillation of india-rubber (*v. Caoutchouc*), when oxidised yields the same products as limonene (Chem. Soc. Trans. 53, 879, and 63, 292).

Cis-trans isomerism has been found by Baeyer to exist among the derivatives of dipentene. When the dihydrochloride is produced by the action of hydrogen chloride on eucalyptol at 0°, it forms a camphor-like mass, which melts at 25°. This is assumed to be the *cis*- form, the already known hydrochloride, m.p. 50°, being the *trans*- form. The corresponding hydrobromides have the melting-points 39° and 64° respectively. Both forms yield the same dipentene, but different terpins (*see Terpin*) (Ber. 1894, 26, 2861).

4. **Sylvestrene group.** Dextrosylvestrene was discovered by Atterberg in Swedish turpentine obtained among the products of destructive distillation of fir-wood (Ber. 10, 1206), also in Russian turpentine oil (Tilden, Chem. Soc. Trans. 33, 80; Wallach, Annalen, 230, 245) in company with *d*-pinene. This variety is dextrorotatory; $[\alpha]_D=66\cdot32^\circ$. *l*-Sylvestrene has since been found in the oleo-resin of *Dacryodes hexandra* (Griseb.) (More, Chem. Soc. Trans. 1899, 75, 718). Sylvestrene has an odour which is different from that of common turpentine, and resembles that of fresh fir-wood. It has a density at 16°=0·8510, at 20°=0·8470. It forms a liquid monohydrochloride and a crystalline dihydrochloride, m.p. 72°, of which $[\alpha]_D=18\cdot99^\circ$, and from which the hydrocarbon may be recovered unchanged by heating with aniline and alcohol. Sylvestrene yields a nitrosochloride $C_{10}H_{16}NOCl$, b.p. 106°–107°, which is strongly dextrorotatory, and from which various

nitrolamines may be formed. Benzylnitrolamine has $[\alpha]_D=185\cdot6°$; m.p. 71°. Sylvestrene tetrabromide [135°] crystallises in monosymmetric tables (Wallach, Annalen, 239, 29).

Sylvestrene is characterised by the production of a blue colour when a solution of it in acetic anhydride is mixed with a drop of concentrated sulphuric acid, other terpenes giving a red or yellow colour.

Carvestrenes. Dihydrocarvone unites with hydrogen bromide forming an additive compound from which, by the action of alkalis, hydrogen bromide is removed and an isomeride of dihydrocarvone $C_{10}H_{16}O$ is produced to which the name *carone* has been given. This is an oil, b.p. about 210°, and yields a liquid oxime. By reduction of the oxime $C_{10}H_{16}:NOH$ a base *carylamine* $C_{10}H_{19}N$ is produced, and from this by heating the hydrochloride in dilute aqueous or alcoholic solution an isomeric base *vestrylamine* is formed. Vestrylamine hydrochloride yields a hydrocarbon when distilled in a current of hydrogen chloride. The crude hydrocarbon yields together with other products a crystalline hydrobromide $C_{10}H_{16}2HBr$, m.p. 48°–50°. This is *carvestrene hydrobromide*, and by the action of quinoline it yields the hydrocarbon which boils at 178° (corr.). It smells like dipentene, becomes resinous on exposure to the air, decolorises potassium permanganate solution instantaneously, and is oxidised by chromic acid at ordinary temperatures. It is optically inactive, and when mixed with acetic anhydride it gives, on adding sulphuric acid, a blue colouration characteristic of sylvestrene. It bears the same relation to sylvestrene as dipentene to limonene (Baeyer, Ber. 1894, 27, 3485).

Carvestrene has more recently been synthesised completely by Perkin and Tattersall (Chem. Soc. Trans. 1907, 91, 480).

iso-*Carvestrene* is also a purely synthetic product (Fisher and Perkin, 1908, 93, 1876). This terpene boils at 176°–177°, it has a pungent odour of lemons, and is oxidised but slowly in the air. A drop of sulphuric acid added to its solution in acetic anhydride produces a violet coloration which rapidly fades. No crystalline hydrochloride or hydrobromide or bromide has been obtained.

With the exception of sylvestrene, the constitution of which still remains to be proved, the terpenes of the *meta*menthadiene series (*see* below) are not known to occur in essential oils.

5. **Terpinolene.** When pinene is mixed with a small quantity of sulphuric or phosphoric acid a considerable evolution of heat is observed, the liquid ultimately becomes optically inactive, and a mixture of hydrocarbons $C_{10}H_{16}$, together with products of polymerisation $(C_{10}H_{16})_n$, results. From the portion which on distillation comes over below 200° may be separated dipentene, terpinolene, and terpinene, together with more or less cymene and small quantities of other compounds. The distillate at about 176°, which was formerly supposed to consist of a single hydrocarbon called 'terpilene,' consists chiefly of dipentene. From the fractions at 180°–190° terpinene and terpinolene may be obtained, though not in a state of purity.

To obtain pure terpinolene γ-terpineol, m.p. 69°–70°, acetate is boiled with quinoline (Baeyer, Ber. 27, 436). Wallach prefers to dissolve terpineol in anhydrous formic acid, whence on the application of gentle heat terpinolene rapidly separates (Annalen, 1909, 368, 1).

Terpinolene boils at about 185°. By uniting with hydrogen chloride and hydrogen bromide it forms the dipentene compounds, m.p. 50° and m.p. 64°. The nitrosochloride is unknown. It forms an optically inactive tetrabromide, which crystallises in monosymmetric tables, m.p. 116°, and is quite distinct from the tetrabromides of dipentene and limonene, especially in its instability, the crystals becoming gradually converted into an opaque mass, with lower melting-points 112° *ca.*

6. **Terpinene.** The product obtained by boiling terpin hydrate with diluted sulphuric acid (Tilden, Chem. Soc. Trans. 33, 250), that formed by the action of slightly diluted sulphuric acid on turpentine (Armstrong and Tilden, *ibid.* 35, 747), also the product of heating the dihydrochloride $C_{10}H_{18}Cl_2$, m.p. 50°, were formerly believed to be identical, and received the name terpinylene or terpilene (Berthelot).

The action of sulphuric or phosphoric acid on terpenes and on terpin is now known to yield, in addition to products of polymerisation (colophene), three distinct hydrocarbons—namely, dipentene, b.p. 175°–176°, terpinolene already described, b.p. 185°, and terpinene (Wallach).

Later researches (Wallach, Annalen, 1908, 362, 285; also 1910, 374, 217) show that the terpinene hitherto obtained is a mixture of two or more isomerides. Ordinary terpinene is believed to contain α-terpinene, boiling at about 179°, β-terpinene, b.p. 173°–174°, and a γ-terpinene or terpinolene. Ordinary terpinene is characterised by the action of nitrous acid which forms a crystalline nitrosonitrite

$$C_{10}H_{16}N_2O_3$$

m.p. 155° (Wallach, Annalen, 239, 33).

β-Terpinene forms a sparingly soluble crystalline tetrabromide $C_{10}H_{16}Br_4$ [154°–155°] and a dihydrochloride, m.p. 52°.

Terpinene-nitrosonitrite · by the action of bases is converted into nitrolamines, for example:

$$C_{10}H_{15}{<}\begin{matrix}NOH\\NH_2\end{matrix}{>}\ \text{m.p. } 116°\text{–}118°,$$

$$C_{10}H_{15}{<}\begin{matrix}NOH\\NHC_2H_5\end{matrix}{>}\ \text{m.p. } 130°\text{–}131°$$

(Wallach, Annalen, 241, 315).

7. **Phellandrene** (Pesci, Gazz. chim. ital. 16, 225). The seeds of *Oenanthe phellandrium* (Linn.), contain about 2·5 p.c. of a volatile oil, of which about 80 p.c. consists of a dextrorotatory terpene, b.p. 171°–172°. The same hydrocarbon is contained, together with anethol, in the oil of bitter fennel, *Fœniculum vulgare* (Mill.) (Wallach, Annalen, 239, 40). It also forms a constituent of oil of elemi, and in small quantity is said to exist in the oils of cassia, cinnamon (Duyk), and sassafras (Power and Kleber).

In the oil of *Eucalyptus amygdalina* (Labill.) Wallach found the isomeric *l*-phellandrene (Annalen, 246, 232).

Phellandrene in either form is easily alterable by the action of acids into dipentene and terpinene; also into a solid polymeride $C_{20}H_{32}$, m.p. 86°.

Phellandrene is specially characterised by the formation of a nitrosonitrite $C_{10}H_{16}\cdot N_2O_3$, first observed by Cahours, afterwards (Zeits.

Chem. 1869, 579) examined by Bunge. Pesci obtained it by the action of a nitrite and dilute sulphuric acid upon the hydrocarbon.

Crude *l*-phellandrene from eucalyptus oil contains two isomeric phellandrenes $C_{10}H_{16}$, together with small quantities of cymene $C_{10}H_{14}$ and cineole $C_{10}H_{18}O$ (Semmler, Ber. 1903, 36, 1749).

d-Phellandrene from elemi oil is identical with *d*-phellandrene from bitter fennel oil but not with *d*-phellandrene from water fennel oil. The former is to be called *d*α-, the latter *d*β-phellandrene. *l*-Phellandrene from eucalyptus is *l*α-phellandrene.

Both *d*α- and *l*α-phellandrene form two nitrites which are separable by crystallisation from acetone and alcohol. The α-nitrite from both melts at 112°–113°, and has approximately the same rotatory power though in opposite directions and opposite in direction to the rotation of the parent hydrocarbon ; thus *d*-phellandrene yields a *l*-nitrite. The β-nitrite from both the phellandrenes melts at 105°, and the rotatory powers of these compounds exhibit similar relations to each other and to the parent.

*d*β-Phellandrene yields similar derivatives (Wallach, Annalen, 1904, 336, 9).

By reduction of phellandrene nitrite, prepared from water-fennel oil by Pesci's method with zinc and glacial acetic acid, a lævorotatory diamine is obtained which boils at 250°–253°. When phellandrene nitrite from eucalyptus is reduced a lævorotatory diamine $C_{10}H_{16}(NH_2)_2$, which is not identical with Pesci's, is formed also boiling at 250°–253°. The hydrochloride of this base melts at 209°–210°. By dry distillation it yields cymene, ammonia and ammonium chloride. Phellandrene nitrite treated with ammonia (Pesci) or with sodium ethoxide (Wallach and Herbig) yields a liquid which boils at 134°–138°, and is identical with the 'nitrophellandrene' described by Pesci (Gazz. chim. ital. 16, 225). Further reduction of the nitrite or of the nitro compound by means of alcohol and sodium leads to the production of tetrahydrocarvone, tetrahydrocarveol, and tetrahydrocarvylamine (Wallach and Herbig, Annalen, 1895, 287, 371).

8. **Fenchene.** Dextrofenchone, $C_{10}H_{16}O$, an isomeride of camphor, is present in fennel oil, and the fraction boiling between 190° and 195° consists chiefly of this compound. Lævofenchone occurs in thuja oil, and is left when the crude ketone is treated with strong nitric acid. By the reduction of *d*-fenchone a lævorotatory fenchylic alcohol is obtained. When this is treated with phosphorus pentachloride, and hydrogen chloride is removed from the product by the action of bases, the hydrocarbon fenchene is obtained. It was originally supposed that this terpene was an individual substance. It appears, however, that fenchylic alcohol gives two fenchylic chlorides and these furnish two fenchenes, one dextro-, the other lævorotatory. As both are derived from dextrofenchone Wallach distinguishes them as D*d*-fenchene and D*l*-fenchene respectively.

From lævofenchone corresponding L*d*- and L*l*-fenchenes have been prepared.

The fenchenes yield an unstable liquid dibromide and are distinguished from other terpenes by comparative indifference toward nitric acid. D*d*-Fenchene is quickly oxidised by a 3 p.c. solution of permanganate, while D*l*-fenchene is slowly oxidised by the same agent. The product is hydroxyfenchenic acid

$$OH{\cdot}C_9H_{14}{\cdot}CO_2H,$$

of which the m.p. and rotation differ according to the origin of the acid.

D*l*-Hydroxy fenchenic acid, m.p. 152°–153° $[\alpha]_D = -56{\cdot}8°$

D*d*- „ „ „ m.p. 138°–139° $[\alpha]_D = +7{\cdot}69°$

L*d*- „ „ „ m.p. 152°–153° $[\alpha]_D = +57{\cdot}3$

r „ „ „ m.p. 142°–143°

(Wallach and Hertz, Annalen, 1898, 302, 371).

A large amount of work has been done on the derivatives of the fenchones, but the formula of fenchone, and consequently of fenchene, is still unsettled (Wallach, *ibid.* 1909, 369, 63). *V.* FENCHONE.

9. **Pinolene.** The mixture of liquid hydrochlorides obtained on saturating crude American pinene with hydrogen chloride when decomposed by bases yields a fraction, b.p. 145°–148°, of constant rotatory power. This is found by Aschan to be a mixture of two isomeric terpenes $C_{10}H_{16}$, of which one is removed by treatment with permanganate, whilst the other remains unattacked. To the former he gives the name α-pinolene, the latter β-pinolene. β-Pinolene is a colourless liquid, b.p. 142°–144°. The hydrochloride, m.p. 25°–26°, is apparently different from the hydrochloride, m.p. 38°, obtained from crude pinolene. Both when heated with aniline and alcohol yield *iso*pinene, b.p. 154°–156°, which forms a crystalline hydrochloride, m.p. 36°–37°. Another hydrocarbon obtained by the action of hydrogen on α-pinene in presence of palladium is described by Zelinsky under the name *iso*pinene (Ber. 1911, 44, 2782). This yields neither hydrochloride nor nitrosochloride. The acid formed by oxidation of α-pinolene by potassium permanganate has been identified as *r*-camphoric acid (Aschan, Chem. Soc. Abstr. 1909, i. 659).

10. **Camphene group.** The monohydrochloride, m.p. 128° (b.p. 210°), of pinene has been long known and was formerly described as 'artificial camphor.' This compound is remarkably stable, but it may be decomposed by heating with sodium stearate or benzoate, with potassium acetate, with alcoholic potash or ammonia, or by a mixture of sodium acetate and caustic soda with alcohol. The resulting hydrocarbon is a camphene, m.p. 51°–52°, b.p. 160°, dextro- or lævo- rotatory, or inactive, according to the nature of the hydrochloride used and the reagent employed (Berthelot, Compt. rend. 47, 266, and 55, 496, 544). The inactive compound seems to be produced when a high temperature is used. A camphene is also formed from bornyl chloride (art. CAMPHORS, vol. i. p. 616) by the action of alcoholic potash (Riban), by the action of water and magnesia (Kachler, Annalen, 197, 86), or by heating with aniline to the boiling-point of the latter (Wallach, *ibid.* 230, 234). Camphene is also formed from camphor chloride (vol. i. p. 618) and from pinene hydrochloride by the action of sodium (Montgolfier, Compt. rend. 87, 84).

In this last case it is accompanied by a hydrocarbon $C_{10}H_{18}$ resembling a paraffin, m.p. 120°, which presents an appearance and odour similar to camphene, but is not attacked by sulphuric or fuming nitric acid.

Camphene is also formed, together with other products, by the action of strong sulphuric acid on turpentine, and constitutes the chief ingredient in the liquid formerly known as 'terebene' (Armstrong and Tilden, Chem. Soc. Trans. 1879, 745).

Camphene occurs in many essential oils, such as oil of rosemary, spike (*Lavandula Spica* [Cav.]), valerian, Siberian fir (*Abies sibirica*), citronella, &c. The melting-point of natural camphene is, however, generally lower than that of the artificial, and Wallach appears to have proved that the derivatives of the camphenes are isomeric, not identical (Annalen, 1907, 367, 72).

Ordinary camphene, active or inactive, possesses a characteristic camphoraceous smell, is soluble in alcohol, and crystallises therefrom in leaflets. It combines with hydrogen chloride to form a chloride $C_{10}H_{17}Cl$, m.p. 157°, which is distinguished from pinene hydrochloride by its inferior stability (Riban, Compt. rend. 80, 1330; Ehrhardt, Chem. News, 54, 239).

Camphene hydrochloride was formerly regarded as identical with bornyl chloride (Kachler and Spitzer, Annalen, 200, 340), but according to Reychler (Bull. Soc. chim. 1896, [iii.] 15, 366), and later Wagner and Brickner (Ber. 1899, 32, 2302), camphene hydrochloride is identical with *iso*bornyl chloride. They regard pinene hydrochloride as the true chloride of borneol. This conclusion is confirmed by Hesse (*ibid.* 1906, 39, 1127).

Camphene does not combine with bromine, and is attacked by it only slowly, with formation of an oily monobromo derivative (230°–240°). Camphene does not combine with nitrosyl chloride. It is converted at about 300° into liquid products which have not been investigated.

When oxidised by chromic acid, ordinary camphene yields camphor, but, according to Marsh and Gardner (Chem. Soc. Trans. 59, 649), when dilute nitric acid is employed as the oxidant a tribasic acid $C_{10}H_{14}O_6$, called by them *camphoic acid*, is produced. Camphoic acid is not produced by the oxidation of camphor or camphoric acid; it has been identified as carboxyl*apo*camphoric acid by Bredt and Jagelki (Chem. Zeit. 1896, 20, 842).

When ordinary camphene is oxidised by neutral permanganate one of the first products formed is camphene glycol $C_{10}H_{16}(OH)_2$, m.p. 200°, together with a ketone, camphenylone $C_9H_{14}O$, m.p. 36°–38°, and a compound $C_{10}H_{16}O_2$, m.p. 169°–170°. When acidified the products of oxidation included camphene camphoric acid $C_{10}H_{16}O_4$, and camphenylic acid $C_{10}H_{16}O_3$. The origin of some of these products is, however, uncertain (*see* Wagner, Moycho and Zienkowski, Ber. 1904, 37, 1032, and Moycho and Zienkowski, Annalen, 1905, 340, 17).

A camphene, m.p. 97·5°–98°, b.p. 150°, together with ordinary camphene, was obtained by Wagner and Brickner (Ber. 1900, 33, 2121) from pinene hydriodide, and is called by them *bornylene* owing to the belief that it is the true relative of camphor and borneol. For the other camphene, m.p. 51°–52°, the name *iso*bornylene is proposed.

It appears, therefore, that at least three camphenes exist which are indistinguishable by appearance and odour, but differ in melting-point and in products of oxidation.

11. **Thujene group.** Several essential oils, such as those of thuja, tansy, wormwood, and sage, contain a ketone $C_{10}H_{16}O$ called thujone or tanacetone. Thujoneoxime, m.p. 54°–55°, is converted into an isomeride, m.p. 90°, by the action of phosphorus pentachloride, and into another optically inactive modification, m.p. 119°–120°, by contact with warm concentrated sulphuric acid. Each of these oximes is reducible to a corresponding base, and the hydrochloride of the base splits under the influence of heat into ammonium chloride and a terpene $C_{10}H_{16}$. The individuality of the hydrocarbons thus formed is still uncertain; by combination with 2 molecules of the hydrohaloids they yield liquid and solid compounds which are now considered to be derivatives of terpinene. Probably isomerisation occurs in most of these transformations (Kondakoff, J. pr. Chem. 1908, [ii.] 77, 135).

12. **Sabinene.** Oil of savin distilled yields about 30 p.c. of a fraction, boiling between 162° and 170°, which consists principally of the hydrocarbon *sabinene* $C_{10}H_{16}$, b.p. 165°–167° (sp.gr. 0·84, mol. refr. 44·9). This yields an oily dibromide, and when oxidised by cold solution of permanganate it yields a glycol $C_{10}H_{18}O_2$, m.p. 54°. An acid sabinenic acid $C_{10}H_{16}O_3$, m.p. 57°, is formed at the same time: it yields a sparingly soluble sodium salt (Semmler, Ber. 1900, 33, 1455). This is an α-hydroxy acid, losing carbon dioxide when oxidised by lead peroxide, to form sabinene ketone $C_9H_{14}O$, b.p. 213°, which is lævorotatory, although sabinene, sabinene glycol and sabinenic acid are all dextrorotatory. Sabinene occurs in the essential oil of Ceylon cardamom and in Majorana oil. When shaken with sulphuric acid sabinene yields a terpin $C_{10}H_{18}(OH)_2$, m.p. 137°, and a terpineol $C_{10}H_{17}{\cdot}OH$, b.p. 209°–212°, which forms a dihydrochloride $C_{10}H_{18}Cl_2$, m.p. 52°. The same *trans*terpinene compound is produced from sabinene by the action of hydrogen chloride in glacial acetic acid. The hydrocarbon is converted into terpinene by boiling dilute sulphuric acid (Wallach, Annalen, 1906, 350, 141).

13. **Dacrydene,** from leaves of *Dacrydium Franklini* (Hook.) (Huon Pine of Tasmania) (b.p. 165°–166°, sp.gr. 0·8524 at 22°, $[\alpha]_D = +14{\cdot}48°$) forms a nitrosochloride, m.p. 120°–121°, but the bromide is liquid and no solid compound with hydrogen chloride has been obtained (H. G. Smith, The Pines of Australia, Sydney, N.S.W., 1910).

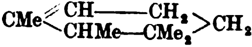
14. **Origanene** from *Origanum spp.* grown in Cyprus. A liquid which boils at 160°–164° at 750 mm., with sp.gr. 0·847 at 16°, a rotation of +1·50° in a 1 dcm. tube and ref. index $n_D = 1{\cdot}480$. It forms a nitrosochloride, m.p. 91°–94°, and from this a nitrolbenzylamine, m.p. 104°–105, and nitrolpiperidide, m.p. 198°, are obtained. The dibromide and hydrobromide are liquid, and a nitrosite has not been obtained. By agitation with dilute sulphuric acid origanene yields ordinary terpin hydrate and the dibromide treated with alcoholic potash yields p-cymene. Oxidation by means of hydrogen peroxide yields succinic acid (Pickles, Chem. Soc. Trans. 1908, 93, 862).

OPEN CHAIN TERPENES $C_{10}H_{16}$.

Myrcene is obtained from oil of bay or sassafras by agitating with soda solution and distilling off the undissolved hydrocarbon under reduced pressure. The following constitution is attributed to it by Barbier (Compt. rend. 1901, 132, 1048) $C_{10}H_{16}$ or

$$CMe_2 : CH{\cdot}CH_2{\cdot}CH : CMe{\cdot}CH : CH_2.$$

Reduced by sodium and alcohol it yields dihydromyrcene $C_{10}H_{18}$, b.p. 171·5°–173·5°, and this when treated with a mixture of acetic and sulphuric acids yields *cyclo*dihydromyrcene



$$CMe\begin{cases} \!\!\!= CH\text{———}CH_2 \\ \!\!\!- CHMe\text{—}CMe_2 \end{cases}\!\!>CH_2$$

, b.p. 169°–172° (Semmler, Ber. 1901, 34, 3122).

Ocimene is the name given by van Romburgh to a hydrocarbon obtained from the leaves of *Ocimum basticum*, and subsequently examined by Enklaar (Proc. K. Akad. Webensch. Amsterdam, 1906, 8, 714). It is said to boil under atmospheric pressure at 172·5°, but is thereby changed into allo-*ocimene*. By reduction with sodium and alcohol ocimene and *allo*ocimene yield the same compound as myrcene. These hydrocarbons are rapidly oxidised in contact with free oxygen.

SESQUITERPENES $C_{15}H_{24}$.

According to Gladstone (Chem. Soc. Trans. 1872, 1), the oils of clove, calamus, cascarilla, patchouli, and cubebs contain a hydrocarbon of this composition. A sesquiterpene has also been found by Wallach (Annalen, 238, 81) in oils of galbanum and savin and in 'huile de cade,' a kind of tar made by distillation of the wood of *Juniperus Oxycedrus* (Linn.). According to the latter chemist, the hydrocarbon *cadinene* obtained from cade or cubebs possesses the following properties. It unites with 2HCl, forming a compound which crystallises from ether in large hemihedral rhombic prisms, m.p. 117°–118°, the solution of which is lævorotatory. Heated with aniline or with sodium acetate the hydrocarbon is set free in a pure state, b.p. 274°–275°; sp.gr. 0·921 at 16°/16°. The hydrobromide $C_{15}H_{24}{\cdot}2HBr$ melts at 124°–125°; the hydriodide $C_{15}H_{24}{\cdot}2HI$ at 105°–106°, with partial decomposition. The hydrocarbon, especially when partially resinified by exposure to the air, gives the following characteristic colour reaction: Dissolved in chloroform or glacial acetic acid, and then shaken up with a few drops of strong sulphuric acid, the liquid assumes an intense green and then blue colour, which when heated passes into red.

Cadinene (lævorotatory) also occurs in the oils of betel, camphor, juniper, asafœtida, coto, and olibanum.

Carophyllene occurs in oils of cloves and copaiba, but has not been obtained pure by fractional distillation. It boils at about 258°–260°. When dissolved in a mixture of glacial acetic and sulphuric acid and the mixture subseq ently steam distilled, a volatile but crystalline alcohol, $C_{15}H_{25}OH$, is formed. The alcohol melts at 96° and boils at 287°–289°. When treated with dehydrating agents the original hydrocarbon is not reproduced, but an isomeride to which the name *clovene* has been given (Wallach and Walker, Annalen, 271, 285).

Caryophyllene produces liquid addition products with the halogen acids, but it forms a solid nitrosochloride, m.p. 158°–160°, and nitrosate, m.p. 147°–150°. The nitrosite forms blue needles, m.p. 107°.

According to Deussen and Lewinsohn (Annalen, 1907, 356, 1) this nitrosochloride is a mixture from which alcoholic ethyl acetate extracts β-caryophyllene nitrosochloride, m.p. 159°, $[\alpha]_D = -98{\cdot}07°$, together with another substance $C_{15}H_{23}O_2N$, m.p. 162·5°–163·5°, $[\alpha]_D = +217{\cdot}2°$. The residue is the α-nitrosochloride, m.p. 177°–179°, which is optically inactive and reacts with benzylamine forming the nitrolamine, m.p. 126°–128°.

Later researches lead to the conclusion that Wallach's caryophyllene is a mixture of two or more isomerides (Deussen, Ber. 1909, 42, 376; Annalen, 1909, 369, 41).

Humulene from oil of hops has been studied by Chapman (Chem. Soc. Trans. 1895, 67, 54, and 780). The sesquiterpene is optically inactive, it boils at 263°–266° and has a vapour density corresponding to $C_{15}H_{24}$. It forms an oily tetrabromide and yields no alcohol when treated in the same manner as caryophyllene. Humulene forms a liquid dihydrochloride, a white crystalline nitrosochloride, m.p. 164°–165°, a nitrosate [162°–163°], and a blue crystalline nitrosite $C_{15}H_{24}N_2O_3$ [*ca.* 121°]. From the nitrosochloride a nitrolpiperidide, m.p. 153°, and nitrolbenzylamine, m.p. 136°, were obtained.

A comparison of caryophyllene and humulene shows that these hydrocarbons are distinct substances (Kremers, Schreiner and James, Pharm. Archives, 1898, i. 209).

Cedrene obtained from oil of cedar is said to boil at 260° (Chapoteaut, Bull. Soc. chim. [ii.] 37, 303). It is lævorotatory $a_D = -17°\ 54'$. It produces unstable compounds with bromine and halogen acids, and when oxidised yields with chromic acid a ketone $C_{15}H_{24}O$ (Rousset, *ibid.* 1897, [iii.] 17, 485). According to Semmler and Hofmann the composition of cedrone is $C_{15}H_{22}O$, b.p. 147°–150°. Cedrene oxidised with permanganate yields cedrene glycol $C_{15}H_{26}O_2$ which crystallises in large prisms, m.p. 160° (Ber. 1907, 40, 3521).

An attempt to prepare from isoprene a polymeride of the composition $C_{15}H_{24}$ proved unsuccessful (Wallach).

Conimene, a hydrocarbon $C_{15}H_{24}$, b.p. 264°, with a pleasant odour, is obtained from the incense-resin (*Protium heptaphyllum* [March]) of British Guiana (Stenhouse and Groves, Chem. Soc. Trans. 1876, i. 175).

POLYTERPENES $C_{20}H_{32}$, &c.

The members of this group may be divided into three classes, viz. (1) Fluid constituents of certain essential oils; (2) products of the polymerisation of terpenes; and (3) caoutchouc and gutta percha.

1. The least volatile portions of many essential oils contain a hydrocarbon probably having the composition $(C_{10}H_{16})_n$, but very little is known concerning these substances. Some of the oils to which the formula $C_{20}H_{32}$ was formerly attributed appear to be sesquiterpenes, the hydrocarbon from balsam of copaiba for example. *See Caryophyllene.*

2. *Colophene* is a viscid yellow fluid, often strongly fluorescent, which begins to boil at

about 300°. It is produced by exposing oil of turpentine or other terpenes to a temperature of about 300° for some hours, or by the action upon them of concentrated sulphuric or phosphoric acid, phosphorus pentoxide, or boron fluoride, &c. The name colophene was given by Deville to the less volatile portion of the product of the action of sulphuric acid on French turpentine, apparently under the impression that it was identical with the oil obtained by distillation of resin. The latter, however, contains oxygen, and exhibits totally different properties.

Colophene obtained by the action of strong sulphuric acid on turpentine oil cannot be distilled without decomposition, even under reduced pressure. The first portions of the distillate contain camphene and dipentene; the boiling-point then rises higher and higher, and even when the temperature approaches that of dull redness a residue is left, which on cooling becomes nearly solid (Armstrong and Tilden, Chem. Soc. Trans. 1879, 748). The portions passing over at 300° and upwards appear to consist of saturated compounds, for they absorb mere traces of hydrogen chloride. Riban has obtained from terebenthene, by the action of antimony trichloride, a solid to which he assigns the formula $C_{40}H_{64}$. This is decomposed by heat, and combines with hydrogen chloride to form two compounds

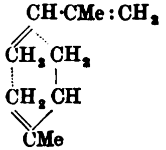
$$C_{40}H_{64},HCl \text{ and } C_{40}H_{64},2HCl$$

(Compt. rend. 79, 389).

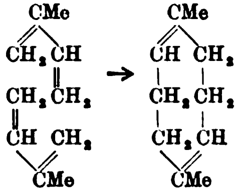
3. *Caoutchouc*. *V*. Rubber.

True rubber is a product which results from the coagulation of the milky juice of trees belonging to several distinct natural orders, as explained in the article referred to. It consists, when pure, of a white, exceeding tough and elastic solid. As usually found in commerce it presents various shades of brown or black colour which are produced by the action of smoke or of atmospheric air on the product of coagulation. Pure india-rubber consists of a hydrocarbon $(C_5H_8)_n$ of high molecular weight, and completely colloidal character. It is insoluble in water and alcohol, but appears to dissolve to a small extent in benzene and its homologues, carbon disulphide, chloroform, and some other liquids forming viscous liquids. The apparent solubility of rubber depends, however, on the treatment to which it has been previously subjected. Rubber unites chemically with many substances, including sulphur and bromine. It combines with the halogen in the proportion of four atoms for every ten atoms of carbon, and therefore seems to have the same capacity of saturation as the limonenes. When destructively distilled it yields a mixture of hydrocarbons consisting of isoprene (b.p. 36°–37°), caoutchene which is identical with dipentene (b.p. 176°), and heveene, which appears to be a variety of colophene (b.p. *ca.* 315°). Rubber, therefore, has the same ultimate composition as the terpenes, and appears to have a formula either $(C_5H_8)_n$ or $(C_{10}H_{16})_n$.

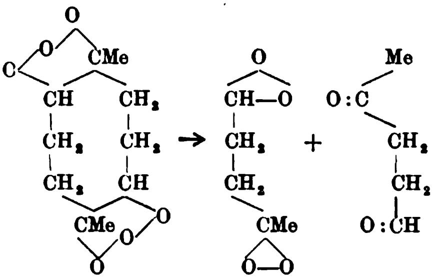
When isoprene is heated to 100°–200° in contact with a small quantity of acetic acid or is kept in contact with a small quantity of air for a long time, it is converted into rubber. Rubber is also formed by contact of isoprene with metallic sodium (Matthews and Strange, Eng. Pat. 24790 [1910]). When heated alone to a temperature of about 280° isoprene is converted into dipentene. Isoprene having been shown by Mokiewsky (Chem. Zentr. 1899, i. 589) to be *β*-methyldivinyl $CH_2:CH{\cdot}CMe:CH_2$, the condensation into dipentene is easily represented by the following formula, in which two molecules of isoprene are supposed to be united at the points indicated by the dotted lines, the valencies adjusting themselves, but without shifting of the hydrogen atoms—



The conversion of isoprene into caoutchouc is, however, open to several explanations. On the one hand, Harries (Ber. 1905, 38, 3985) assumes the formation of an octadiene as the first product of the union of two molecules of isoprene—



This hypothesis is chiefly based on the fact that when rubber, in chloroform solution, is brought into contact with ozone a compound is formed with two molecules of that substance. This compound has the *molecular* formula $C_{10}H_{16}O_6$. When boiled with water it splits up into lævulic aldehyde or lævulic acid and lævulic aldehyde diperoxide—



Diozonide. Diperoxide. Lævulic aldehyde.

On the other hand, it has been suggested with greater probability that the caoutchouc molecule consists of long chains. One form of hypothesis (Pickles, Chem. Soc. Trans. 1910, 1088) is expressed in the following formula in which an indefinite number of C_5H_8 groups may be linked together—

$$CH_2:CMe{\cdot}CH:CH_2 + CH_2:CMe{\cdot}CH:CH_2, + \&c.$$

becoming

$$\ldots CH_2{\cdot}CMe:CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe:CH{\cdot}CH_2,\ldots \&c.$$

The direct conversion of isoprene into rubber with its indefinitely large molecule is in this way easily represented, and it may be remarked that the ready depolymerisation of rubber into isoprene by heat seems to support the view that it is directly resolved into C_5H_8 groups, and not into groups of $C_{10}H_{16}$. The dipentene which accompanies isoprene in the destructive distillation of rubber is probably a secondary product of the polymerisation of isoprene by heat.

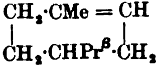
One great objection to Harries' formula is the fact that it represents the chemical molecule of rubber as consisting of $C_{10}H_{16}$, whilst it is certain that the actual physical molecule of the colloid is very much more complex, and there seems no way of accounting for the chemical association together of a number of octadiene molecules without loss of free valency, and hence reduction of the saturating power.

Hydroterpenes.

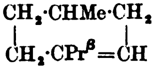
Menthene $C_{10}H_{18}$. This compound stands in the same relation to menthone $C_{10}H_{18}O$ and menthol $C_{10}H_{19}\cdot OH$, as does camphene to camphor and borneol. It is obtained by treating menthol with phosphorus pentoxide at the common temperature or with zinc chloride at the boiling-point (Brühl and others, 1892, Ber. 25, 142). Menthene boils at 167°. It forms a nitrosochloride, m.p. 113°, and an oily dibromide.

Carvomenthene $C_{10}H_{18}$. Dihydrocarveol produced by the reduction of carvone, by means of sodium and alcohol, yields with acetic anhydride an acetate, b.p. 232°–234°. This takes up hydrogen iodide, and the resulting hydriodide, when reduced with zinc-dust and acetic acid, yields tetrahydrocarveol acetate which on saponification[4] yields tetrahydrocarveol. If this compound is converted into its hydrobromide, and the latter is heated with quinoline, *carvomenthene*, b.p. 175°–176° is obtained. This is isomeric with the menthene obtained from menthol (Baeyer, Ber. 1893, 26, 820). Carvomenthene obtained by heating carvomenthyl chloride or bromide with alcoholic potash appears to be divisible into two portions by fractional distillation, about 90 p.c. of the whole distilling at 17-°–174·5°, the rest at a few degrees higher (Kondakoff and Lutschinin, J. pr. Chem. 1899, [ii.] 60, 257).

The following formulæ are attributed by Baeyer (*l.c.*) to carvomenthene and menthene respectively—



$$\begin{array}{l} CH_2\cdot CMe = CH \\ | \qquad\qquad\quad | \\ CH_2\cdot CHPr^{\beta}\cdot CH_2 \end{array}$$



$$\begin{array}{l} CH_2\cdot CHMe\cdot CH_2 \\ | \qquad\qquad\quad | \\ CH_2\cdot CPr^{\beta} = CH \end{array}$$

Action of Heat upon the Terpenes.

The terpenes heated to temperatures of 250°–300° lose their rotatory power and are slowly polymerised (Berthelot, Ann. Chim. Phys. [iii.] 39, 5). When ordinary turpentine oil is passed through a tube heated to redness scarcely visible in the dark, it yields a quantity of gas and various liquid products, of which the most important are isoprene C_5H_8, dipentene $C_{10}H_{16}$, *p*-cymene $C_{10}H_{14}$, and colophene $(C_{10}H_{16})_n$, with relatively small quantities of benzene, toluene, and *m*-xylene (Tilden, Chem. Soc. Trans. 1884, 45, 410). At higher temperatures no isoprene is obtained, but a larger quantity of gas, and the most volatile liquid product is benzene, which is accompanied by some of its homologues, besides naphthalene, anthracene, &c. (Schultz, Ber. 1877, 10, 113).

It has been found by Staudinger and Klever that limonene or dipentene, when diluted with an indifferent gas, such as nitrogen, or under reduced pressure, yields a much larger quantity of isoprene, amounting to 60 p.c. and upwards. The temperature required is produced by a platinum spiral electrically heated to redness (Ber. 44, 2212). The isoprene thus obtained is said to be purer than the isoprene previously obtained. According to these authors the yield of isoprene under the same circumstances is much smaller when pinene, camphene, terpinene, or terpinolene is employed.

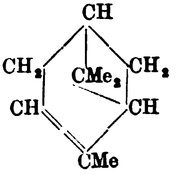
A convenient arrangement of the spiral within a flask connected with a vertical condenser has been described by Harries and Gottlob (Annalen, 1911, 383, 228). The unchanged terpene drops back into the flask, the isoprene passing off into a properly cooled receiver.

Camphene, when heated, yields other products which have not been fully examined.

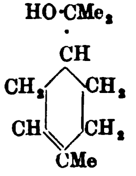
Constitution of the Terpenes.

The terpenes generally exhibit many of the properties of olefinic hydrocarbons combining with two or four molecules of bromine, with one or two molecules of hydrogen chloride, and with one or two molecules of water. They also form characteristic compounds with nitrosyl chloride. By the loss of two atoms of hydrogen the terpenes yield a considerable, though varying, amount of common cymene, *methyl*-p-iso*propyl benzene* (G. Williams, Proc. Roy. Soc. 10, 516; Oppenheim, Ber. 5, 628; Wright, Chem. Soc. Trans. 1873, 686). All the terpenes, when exposed to heat, polymerise into viscous products, and at a temperature of about 400° yield a considerable quantity of isoprene $CH_2:CH\cdot CMe:CH_2$, a hydrocarbon, which by prolonged heating at a lower temperature is converted into limonene $C_{10}H_{16}$. Pinene is distinguished by the readiness with which it undergoes isomeric change, especially under the influence of diluted acids, whereby it is converted into terpin, terpineol, and dipentene. The product of its union with hydrogen chloride is, according to conditions, either bornyl chloride $C_{10}H_{17}Cl$ or dipentene dihydrochloride $C_{10}H_{18}Cl_2$, and from neither of these can pinene be regenerated. The only compound from which pinene can be recovered is the nitrosochloride $(C_{10}H_{16}NOCl)_2$, as already mentioned (*v.* Pinene).

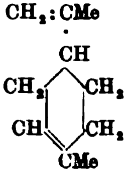
These facts can be accounted for by the following formulæ which were proposed in 1894 by G. Wagner (Ber. 27, 1636).



Pinene.

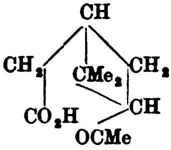


Terpineol.

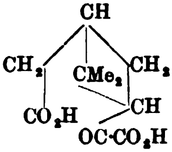


Limonene.

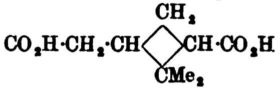
The dimethylated tetramethylene ring in the formula of pinene is very readily broken up by the action of dilute acids, which cause the addition of the elements of water as shown above, yielding terpineol, or the closely connected glycol, terpin. It is, however, very stable under the action of neutral or alkaline oxidising agents such as permanganate. This tetramethylene group has been named 'picean' by Baeyer. The products of the oxidation of pinene by permanganate include α-pinonic acid $C_{10}H_{16}O_3$—



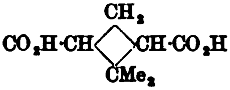
and dibasic pinoyl-formic acid $C_{10}H_{14}O_5$.



These compounds retain the picean ring which is capable of hydrolytic rupture in both of them, much as in the case of pinene itself. Further oxidation leads to the production from both of these acids of the same pinic acid—

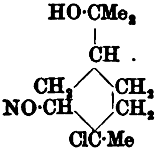


and ultimately of norpic acid—

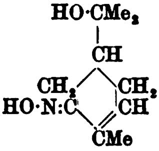


The constitution of limonene was first indicated by the discovery that the nitroso compound $C_{10}H_{15}NO$, obtained from the nitrosochloride $C_{10}H_{16}NOCl$ by the action of alkali, is identical with carvoxime $C_{10}H_{14}:NOH$ (Goldschmidt and Zürrer, Ber. 18, 2220).

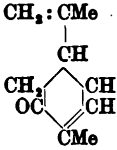
The nitrosochloride of terpineol is also convertible into carvone by removing the elements of hydrogen chloride so as to produce the oxime of the hydroxy ketone from which carvone is obtained by the action of acids (Wallach).



Terpineol nitrosochloride



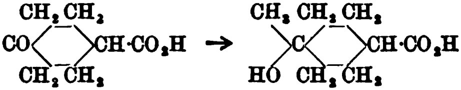
Oxime



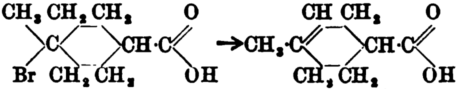
Carvone

More recently the formulæ of terpineol and limonene have been completely established by synthesis, the principal steps in the process being the following:—

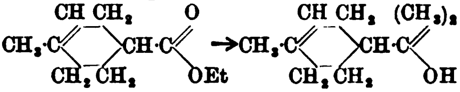
The esters of β-iodopropionic acid and sodiocyanacetic acid are brought together and after interaction the product is hydrolysed. Pentane-αγε-tricarboxylic ester is thus obtained from which δ-ketohexhydrobenzoic acid is formed by treatment with acetic anhydride and distillation. The ester of this acid in contact with magnesium methyl iodide yields δ-hydroxyhexhydro-*p*-toluic acid—



Hydrogen bromide converts this toluic acid into the corresponding bromo derivative, which, when treated with weak alkalis or pyridine, loses hydrogen bromide and yields Δ'-tetrahydro-*p*-toluic acid—



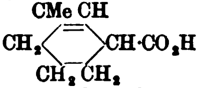
The ester of this unsaturated acid is converted by magnesium methyl iodide in ethereal solution into inactive *terpineol*—



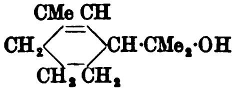
By the simple abstraction of water from terpineol by means of potassium hydrogen sulphate dipentene results, and hence the position of the second ethylenic bond in that compound is determined. These formulæ are identical with those proposed by Wagner (W. H. Perkin, junr., Chem. Soc. Trans. 1904, 654).

Optically active *d*- and *l*-terpineols were afterwards prepared by Perkin and Fisher (*ibid.* 1908, 1871).

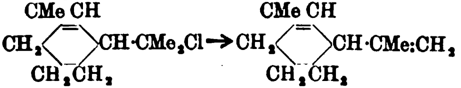
The great majority of the terpenes found in nature are compounds in which the side chains occupy the *para-* position as in limonene. The sylvestrene (*q.v.*) discovered by Atterberg in Swedish turpentine has, however, been shown by Perkin to be a *meta-* compound. Proceeding from Δ'-tetrahydro-*m*-toluic acid—



a dextrorotatory hydrocarbon identical with natural sylvestrene has been built up by synthesis. The *d*-acid was first isolated from the inactive mixture by means of brucine and the ester was made to interact with magnesium methyl iodide. The resulting *d*-dihydrocarvestrenol is the representative of terpineol in the meta series and is represented by the following formula—

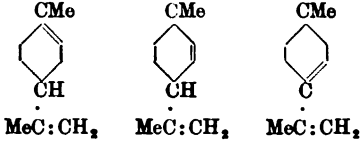


By the action of hydrogen chloride it yields *d*-carvestrene dihydrochloride which melts at 72° and is identical with the hydrochloride obtained from natural sylvestrene. The hydrocarbon is isolated from the hydrochloride by heating it with aniline—

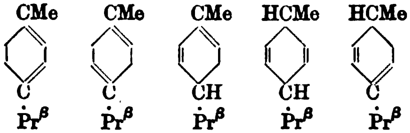


(Perkin, Chem. Soc. Proc. 1910, 97).

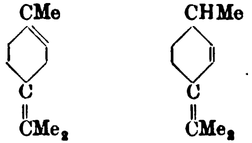
It is now apparent that the formulæ of some of the other natural terpenes are probably closely related to the formula of limonene. Thus there may be theoretically three compounds containing ·Me and ·CMe : CH_2 in the para- position, while there is one double bond in the ring—



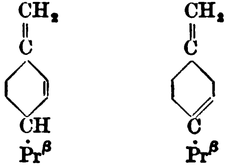
There may also be five isomeric dihydrocymenes—



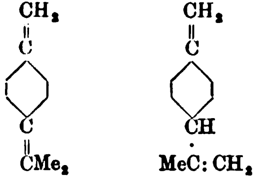
There may be two other isomerides of the type—



Two more of the following form—



And lastly two isomerides in which the double linking is wholly external to the ring—



Of some of these there are also geometrical isomeric forms.

It is sometimes convenient to adopt a system of numbering the carbon atoms as introduced by Baeyer in the case of the terpenes. The para- series is based on the formula of hexhydrocymene—

According to this system dipentene, for example, is Δ1·8(9)-*p*-menthadiene and terpineol is Δ1-*p*-menthenol 8.

The hydrocarbons enumerated above are only the varieties in which the *para-* position is assumed by the side chains, but these and others already known may be arranged under the following divisions.

MENTHADIENES $C_{10}H_{16}$.

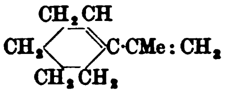
I. Derivatives of cyclohexene—
  1. *Para-*. Limonene and dipentene, terpinene, phellandrene.
  2. *Meta-*. Sylvestrene.
  3. *Ortho-*. Synthetical products unknown in nature.

II. Derivatives of *cyclo*hexene with bridged rings—
  1. *Para-* containing two pentamethylene rings: fenchene, camphene (?).
  2. *Meta-* containing one tetramethylene ring: pinene.
  3. *Meta-* containing one trimethylene ring: sabinene, thujene.

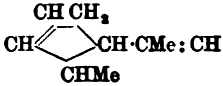
III. Olefinic terpenes with open chains. Myrcene, ocimene.

The production of a terpene of the *ortho-* type has been accomplished by Ray and Perkin (Chem. Soc. Trans. 1905, 1066).

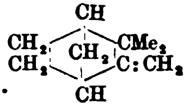
Perkin has also made progress in the synthesis of lower homologues of the terpenes. The hydrocarbons C_9H_{14} prepared belong to two types. One of these is derived from *cyclo*hexane containing no methyl group in the ring (Matsubara and Perkin, *ibid.* 1905, 661).



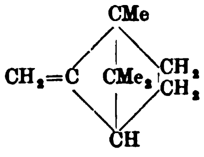
The other is framed on a cyclo*pentene* containing a methyl group (Haworth and Perkin, *ibid.* 1908, 573).



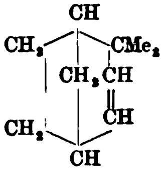
Among the questions which remain unsettled is the identity of the terpinenes, concerning which a summary of researches has been published by Wallach (Annalen, 1910, 374, 217). The constitution of the solid terpene, camphene, is also a subject of dispute. The formula assigned to it long ago by Wagner, namely—



(Ber. 1900, 33, 2121) is not found to account for all the products of oxidation of the hydrocarbon. An alternative formula has been proposed by Semmler (Ber. 1900, 33, 3420), as follows—



and another more recently by Aschan (Annalen, 1910, 375, 336).



On the other hand, according to Auwers (Annalen, 1912, 387, 40) the specific refraction of camphene is definitely in favour of Wagner's formula given above. See also Haworth and King, Chem. Soc. Trans. 1912, 101, 1975.

For the optical properties of the terpenes, such as specific rotatory power and especially refractivity, and their relation to the constitution of the hydrocarbons, a useful summary will be found in Smiles' Relations between Chemical Constitution and Physical Properties (Longmans' Text-books of Physical Chemistry).

OXIDISED COMPOUNDS RELATED TO THE TERPENES.

1. **Absinthol** $C_{10}H_{16}O$, identical with thujone.
2. **Borneol** $C_{10}H_{17}OH$, *v.* vol. i., CAMPHORS.
3. **Cajeputol** $C_{10}H_{18}O$, identical with cineol.
4. **Carveol** $C_{10}H_{16}O$, *v.* vol. i., CAMPHORS.
5. **Carvone** $C_{10}H_{14}O$, *v.* vol. iii., KETONES.
6. **Camphor** $C_{10}H_{16}O$, *v.* vol. i.
7. **Cineol** $C_{10}H_{18}O$, *v.* vol. i., CAMPHORS, SANTONICA.
8. **Citronellol** $C_{10}H_{19}\cdot OH$, an alcohol similar to geraniol found in citronella and rose oils.
9. **Coriandrol** $C_{10}H_{17}OH$, identical with *d*-linalool.
10. **Eucalyptol** $C_{10}H_{18}O$, identical with cineol.
11. **Fenchone** $C_{10}H_{16}O$, *v.* vol. iii., KETONES.
12. **Geraniol** $C_{10}H_{17}\cdot OH$. Indian oil of geranium (*Andropogon Schœnanthus* [Linn.]) consists chiefly of this compound (Semmler, Ber. 23, 1098, 2965, 3556; 24, 682).

Geraniol is an optically inactive compound with a smell of roses. It boils at 229°–230°.

When oxidised by chromic acid it yields the corresponding aldehyde, citral or geranaldehyde $C_{10}H_{16}O$. Further oxidation yield geranic acid $C_{10}H_{16}O_2$, which is monobasic.

Geraniol heated with potassium hydrogen sulphate yields a terpene, geraniene, which boils at 172°–176°.

13. **Citral,** the aldehyde, occurs as a natural constituent of the oil of lemon, lemon grass, and many other essential oils. It boils at 228°–229° under ordinary pressure, and is optically inactive. It unites with four atoms of bromine, and is characterised by the readiness with which by the action of potassium hydrogen sulphate it yields ordinary cymene. In other respects it gives the usual reactions of aldehydes. It reduces silver solutions, combines to form a crystalline compound with sodium hydrogen sulphite, and reproduces the colour of rosaniline from a sulphite solution.

It also yields an aldoxime and a semicarbazone.

Geranic acid, which is best formed from the nitrile by boiling with potash, is a colourless oil possessing an odour like that of the higher fatty acids. When distilled under ordinary pressure it yields carbon dioxide and a hydrocarbon, geraniolene C_9H_{16}, which boils at 142°–143°. Geraniolene forms a liquid tetrabromide $C_9H_{16}Br_4$.

14. **Linalool** $C_{10}H_{17}\cdot OH$. This substance is very widely distributed in essential oils derived from various plants. The name has reference to the wood of the lignum aloes (*Aquilaria Agallocha* [Roxb.]), in which it was originally recognised, but the alcohol or its acetate is found in the oils of lavender, bergamot, petit grain (leaves and shoots of orange) neroli, &c. It is distinguished from geraniol, with which it is isomeric, by its lower boiling-point and by its lævorotatory action on the polarised ray. The boiling-point under atmospheric pressure is about 198°–199°.

15. **Coriandrol** is dextrorotatory linalool (Semmler, Ber. 24, 206; Tiemann and Semmler, *ibid.* 26, 2713).

Linalool treated with acetic anhydride yields, at the ordinary temperature, an acetate which regenerates linalool on saponification, but if the acetate is heated to 100° and upwards it undergoes isomeric change, and on saponification it yields geraniol (Bouchardat, Compt. rend. 116, 1253).

d- or *l*-Linalool and geraniol, shaken with dilute sulphuric acid, are converted almost quantitatively into terpin hydrate (Tiemann and Schmidt, Ber. 1895, 28, 2137).

Linalool on oxidation by means of acid reagents yields citral, the aldehyde of geraniol.

The following constitution is assigned to these compounds (Tiemann and Semmler, Ber. 1895, 28, 2126).

Linalool

$Me_2C : CH\cdot CH_2\cdot CH_2\cdot CMe(OH)CH : CH_2$

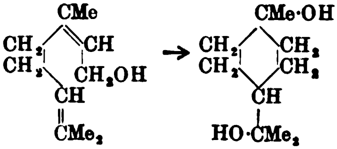
Geraniol

$Me_2C : CH\cdot CH_2\cdot CH_2\cdot CMe : CH\cdot CH_2\cdot OH$

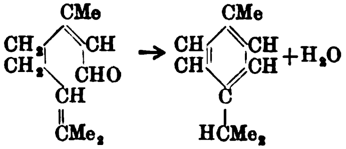
Citral

$Me_2C : CH\cdot CH_2\cdot CH_2\cdot CMe : CH\cdot CHO$

These open chain compounds are, however, readily converted into cyclic compounds, especially by the action of acids, for example, in the production of terpin from geraniol—



and in the production of cymene from citral.



16. **Menthol** $C_{10}H_{19}OH$ *v.* vol. i., CAMPHORS.
17. **Pinole** $C_{10}H_{16}O$, *see* under *Pinene.*
18. **Pulegone** $C_{10}H_{16}O$, *v.* vol. iii., KETONES.
19. **Sobrerol** $C_{10}H_{18}O_2$, *see* under *Pinene.*
20. **Sobrerone** $C_{10}H_{16}O$, identical with pinole.
21. **Tanacetone** $C_{10}H_{16}O$, *v.* vol. iii., KETONES.
22. **Terpineol** $C_{10}H_{17}OH$. *Terpinol* was the name given by List (Annalen, 1848, 67, 362) to the liquid obtained by the action of dilute acids upon terpin hydrate.

When crystallised terpin is boiled with water and a small quantity, say 1 p.c., of hydrochloric acid is added, the crystals disappear and a turbid fluid results, from which by distillation an oily liquid, lighter than water and possessing a peculiar fragrant odour, resembling that of lilac, is obtained. When the oil is dried and distilled, the whole comes over, with the exception of a few drops at first, between 205° and 215°. Treated with sodium, terpineol dissolves one atom of the metal; and by contact with excess of hydrochloric acid it becomes coloured deep purple, but the colour disappears and the whole is converted into dipentene hydrochloride $C_{10}H_{18}Cl_2$ (m.p. 50°); when mixed gradually with a nearly equal volume of sulphuric acid diluted with half its bulk of water, very little heat is evolved, but solution is complete, and on adding to the mixture three or four volumes of water a mass of crystallised terpin hydrate is obtained. Terpineol is also quickly converted into terpin hydrate by a mixture of nitric acid and alcohol (Tilden, Chem. Soc. Trans. 1878, 247; 1879, 287). Terpineol absorbs two atoms of bromine (Tilden, *ibid.* 1888, 882), and it is, therefore, an unsaturated tertiary alcohol $C_{10}H_{17}(OH)$, of which the corresponding glycol is terpin $C_{10}H_{18}(OH)_2$. By *boiling* with potassium hydrogen sulphate terpineol splits into water and dipentene.

Terpineol yields a nitrosochloride

$$C_{10}H_{18}O{\cdot}NOCl$$

from which a piperidide [m.p. 159°–160°] and anilide [m.p. 155°–156°] are obtainable (Wallach and Kerckhoff, Annalen, 1893, 275, 103).

More recent researches have shown that liquid terpineol obtained as described or by hydrolysis of the corresponding acetate contains two distinct compounds. Bouchardat and Voiry (Compt. rend. 1887, 104, 996) were the first to obtain crystals by cooling. The m.p. was found to be 35° (Wallach). Distilled under reduced pressure liquid terpineol yields two principal fractions, boiling at 212°–215° and 218°–220° at ordinary pressure. Both solidify on cooling, the former having the m.p. 32°–33°, and the latter 35°–36°.

The terpineol [m.p. 35°–36°] forms a nitrosochloride [m.p. 122°], which yields the piperidide mentioned above [m.p. 159°–160°]. Its phenylurethane $NHC_6H_5{\cdot}CO{\cdot}OC_{10}H_{17}$ melts at 112°–113°. The new terpineol [m.p. 32°–33°] gives a nitrosochloride [m.p. 102°–103°], but does not readily yield a piperidide. The phenylurethane melts at 85°.

Both these terpineols have been produced synthetically by W. H. Perkin (Chem. Soc. Trans. 1904, 85, 654), starting from ethyl β-iodopropionate and ethylsodiocyanoacetate. Their constitution is therefore now fully established. *See* below.

These compounds are optically inactive, but active terpineols have been obtained from other sources, *l*-linalool $C_{10}H_{18}O$, when heated with acetic acid containing a small quantity of sulphuric acid yields *d*-terpineol, together with geraniol, while in similar way *d*-linalool yields *l*-terpineol (Stephan, J. pr. Chem. 1898, [ii.] 58, 109).

Optically active terpineols have been produced synthetically by Perkin and Fisher (Chem. Soc. Trans. 1908, 93, 1871) by resolving the corresponding *dl*-cyclohexene carboxylic acid by means of brucine or strychnine.

Active terpineols also occur in certain essential oils, *e.g.* oil of *Asarum canadense* [Linn.] (Power and Lees, *ibid.* 1902, 81, 63).

23. **Terpin** $C_{10}H_{18}(OH)_2$ and **Terpin hydrate** $C_{10}H_{18}(OH)_2{\cdot}H_2O$. This compound is occasionally found in old samples of turpentine oil containing a little water, and in furniture polish of which turpentine is an ingredient. It is easily obtained by the action of a mixture of nitric acid and alcohol upon turpentine oil (Wiggers, Annalen, 1846, 57, 251). Hempel recommends (*ibid.* 180, 71) 4 parts oil of turpentine to 1 part of alcohol and 1 part of nitric acid. In any case, the mixture is shaken up at intervals until in the course of about two days the smell of turpentine has disappeared. The liquid is then poured out into shallow dishes, a little alcohol being added occasionally as long as crystals are deposited (Tilden, Chem. Soc. Trans. 33, 247). No crystals are formed under the same circumstances from the limonenes, but from the hydrochlorides of these hydrocarbons terpineol, and hence terpin is easily obtained by the action of water or dilute alcohol.

Terpin hydrate [116°–117°] dissolves in about 200 parts of cold, and in 22 parts of boiling, water. It is easily soluble in alcohol, but not in petroleum. It is optically inactive, and is chemically saturated. Anhydrous terpin melts at 104°–105°, and boils at 258°. The crystals have been examined by List (Annalen, 67, 362), by Rammelsberg (Poggendorff's Annalen, 63, 570), and by Maskelyne (Phil. Mag. 1879, 132).

Exposed to hydrogen chloride the crystals deliquesce, become purple, and finally give a mass of the colourless dipentene dichloride $C_{10}H_{18}Cl_2$ [m.p. 50°]. Boiled with water slightly acidified with hydrochloric or sulphuric acid it yields terpineol. Boiled with moderately strong sulphuric acid it yields a mixture of dipentene, terpinene, and terpinolene.

Cis- and *trans-* terpins have been obtained by Baeyer from the corresponding *cis-* and *trans-* hydrobromides of dipentene (Ber. 1894, 26, 2861). *Cis*dihydrobromide when treated successively with silver acetate and alcoholic potash gives ordinary terpin. The *trans-* dihydrobromide, when similarly treated, yields the *trans*-terpin which crystallises without water, melts at 156°–158°, and boils at 263°–265°.

24. **Thujone** $C_{10}H_{16}O$, identical with tanacetone. W. A. T.

TERPENYLIC ACID *v.* Lactones.

TERRA ALBA *v.* Gypsum.

TERRA CATECHU. Syn. with Catechu (*q.v.*).

TERRA CHE BRUCIA or *Val d'Arno Superiore Resin v.* Resins.

TERRA DI SIENNA. *Raw Sienna v.* Pigments.

TERRA FOLIATA TARTARI. Potassium acetate.

TERRA JAPONICA. Syn. with Catechu (*q.v.*).

TERRA LEMNIA *v.* Lemnian earth.

TERRA MIRACULOSA. An old name for bole (*q.v.*).

TERRA MURIATICA. An obsolete name for magnesia.

TERRA PONDEROSA. An old name for baryta (*q.v.*).

TERRA UMBRA. Umber (*q.v.*).

TESTADEN *v.* Synthetic drugs.

TETRADECYLMALONIC ACID $C_{17}H_{32}O_4$. Prepared by heating α-cyanopalmitic acid with alcoholic potash (Hell and Iordanoff, Ber. 1891, 991), m.p. 117°–118°.

TETRADYMITE *v.* Tellurium.

TETRAETHYL- and **TETRAMETHYL-DIAMINOBENZOPHENONE** *v.* Ketones.

TETRAHEDRITE *v.* Fahl-ore.

TETRAHYDROXYBENZENE *v.* Phenol and its homologues.

TETRAIODOPYRROLE *v.* Iodole.

TETRAKETONES *v.* Ketones.

TETRAMETHYLAPIONOL *v.* Phenol and its homologues.

TETRAMETHYLBENZENES *v.* Cymenes.

TETRAMETHYLHYDROXYBENZENE *v.* Phenol and its homologues.

TETRAMETHYLSAFRANINE *v.* Azines.

TETRATHIONIC ACID *v.* Sulphur.

TETRAZO- COMPOUNDS *v.* Disazo- and Tetrazo- compounds.

TETRONAL (*diethylsulphonediethylmethane* or *ethyl sulphonal*) $(C_2H_5)_2C(SO_2C_2H_5)_2$ is prepared like sulphonal from diethylketone and ethyl mercaptan (Baumann and Kast, Zeitsch. physiol. Chem. 14, 61; D. R. P. 49366; Frdl. 1887–1890, ii. 523). It forms colourless, odourless, glistening leaflets, or radiating almost round fibrous groups similar to urea oxalate; m.p. 85°, soluble in 450 parts of cold water, but more readily soluble in boiling water, in alcohol, and in ether. It is employed in medicine as a substitute for sulphonal.

Adulteration of tetronal and trional with sulphonal, which is cheaper than the two former, may be detected by treating the suspected sample with ether, in which sulphonal is much less soluble, the residue will, therefore, contain sulphonal which may be detected by its melting-point and its known reactions (Gabutti, J. Pharm. Chim. 1907, 25, 183); *v.* Sulphonal.

TETRYL *v.* Butyl.

THALLIUM, sym. Tl., at.wt. 204·0, was discovered spectroscopically by Crookes in 1861 (Chem. News, 1861, 3, 193) in a seleniferous deposit from a sulphuric acid manufactory. It occurs in many iron and copper pyrites, in some micas, in zinc blendes, in the minerals *marcasite*, *hæmetite*, *crookesite* $(CuTlAg)_2Se$, *lorandite* ($TlAsS_2$), *orbaite* $TlAs_2SbS_5$, and in various other iron and manganese ores (Igelström, Z. Kryst. Min. 1895, 25, 94; Antipoff, J. Russ. Phys. Chem. Soc. 1896, 28, 384; Hartley and Ramage, Chem. Soc. Trans. 1897, 533). It also occurs in small quantities in various mineral springs.

Its presence has been observed in crude zinc (Kosmann) and in platinum and its ores (H. N. Warren, Chem. News, 1887, 55, 241).

Thallium is prepared from flue dust by boiling it with dilute sulphuric acid and precipitating the chloride or iodide by treatment with hydrochloric or hydriodic acid, after which the metal can be obtained by electrolytic deposition, by the action of potassium cyanide or by electrolysis (Bunsen, Phil. Mag. 1865, [iv.] 29, 168; Foerster, Zeitsch. anorg. Chem. 1897, 15, 71). Traces of lead, tin, copper, and aluminium occur as impurities in commercial thallium (Pollock, Sci. Proc. Roy. Dublin Soc. 1909, 11, 338).

Thallium is a bluish-white, lead-like, crystalline, extremely soft metal, malleable, but of low tenacity. It exists in two modifications, the transition temperature being 226°. Its sp.gr. is 11·85, its m.p. 303° (Petrenko, Zeitsch. anorg. Chem. 1906, 50, 133), its b.p. in vacuum 818° (Krafft and Knocke, Ber. 1909, 42, 202); at ordinary pressure 1515±2° (Isaac and Tammann, *ibid.* 1907, 55, 58); but its b.p. should be 1462° at 760 mm. Its vapour density is 14·25 at 1728°. It commences to volatilise at 174° *in vacuô*. At a high temperature it may be distilled in a current of hydrogen. When heated it burns with a beautiful green flame, and its flame spectrum is characterised by a single green line.

Thallium oxidises before the blowpipe. It dissolves readily in dilute nitric and sulphuric acids, but more slowly in hydrochloric acid, and at a red heat decomposes water.

Thallium and its salts are very poisonous (Curci, Chem. Zentr. 1895, ii. 999; Swain and Bateman, J. Biol. Chem. 1910, 7, 137). Thallium forms alloys with a large number of metals, and an amalgam with mercury.

Compounds.—Thallium forms two series of compounds—

(1) Thallic (TlX_3) compounds in which the metal is trivalent, corresponding to its position in the aluminium group. Like the compounds of aluminium, the thallic salts undergo hydrolysis in aqueous solution and form complex salts more readily than the corresponding thallous compounds (Spencer and Abegg, Zeitsch. anorg. Chem. 1905, 44, 379). Metallic thallium reduces the thallic salts to the thallous condition. In the absence of oxidising agents, even in the presence of thallous salts, thallic salts give the blue coloration of indophenols when α-naphthol and dimethyl-*p*-phenylene diamine are added to an alkaline solution of the salt (Marino, Gazz. chim. ital. 1907, 37, i. 55).

(2) Thallous (TlX) compounds in which thallium is monovalent. The thallous salts closely resemble the salts of the alkali metals; thus the hydroxide and carbonate are readily soluble and give an alkaline aqueous solution. Many of the thallous salts, like the sulphate phosphate, &c., are isomorphous with the corresponding potassium salts and give double salts with platinic chloride Tl_2PtCl_6. The alum $Tl_2SO_4Al_2(SO_4)_3,24H_2O$ and other double sulphates are also closely analogous to the corresponding potassium salts. The thallous halides and sulphides, on the other hand, resemble the corresponding lead and silver salts.

Thallous salts react with a clear aqueous solution of antimony chloride and potassium iodide, giving a characteristic voluminous orange precipitate of the compound $3TlI,2SbI_3$ (Ephraim, Zeitsch. anorg. Chem. 1908, 58, 353).

Oxides. Thallium trioxide (thallic oxide) Tl_2O_3 is formed when an alkaline solution of a thallous salt is treated with 3–5 p.c. solution of hydrogen peroxide. When the precipitation is made in the cold, the oxide is brown, is readily soluble in acids, and has sp.gr. 9·65 at 21°, but when the solutions are hot, the oxide is black, is sparingly soluble in acids, and has the sp.gr. 10·19 at 22°. The brown oxide is partly reduced when boiled with water, but the black oxide remains unchanged. At 100° the brown slowly changes into the black variety, and at 520° this change is complete within 24 hours (Rabe, Zeitsch. anorg. Chem. 1906, 48, 427; *ibid.* 50, 158; *ibid.* 1907, 55, 130). The crystalline oxide obtained by heating the nitrate has sp.gr. 9·97 (Thomas, Compt. rend. 1904, 138, 1697; *see* also Fortini, Gazz. chim. ital. 1905, 35, ii. 450).

Thallium monoxide (thallous oxide) Tl_2O is obtained by exposing the metal to the air or by heating the corresponding hydroxide at 100° out of contact with air. It is a black powder, m.p. 300°, readily dissolving in water with formation of the *hydroxide* TlOH, which crystallises with 2 molecules of water in yellow needles. The hydroxide turns turmeric brown, and finally destroys the colouring matter (Erdmann, J. pr. Chem. 1863, 89, 381).

The *oxide* $(TlO)_x$, probably Tl_2O_3,Tl_2O, is prepared by adding 175–200 grms. of 20 p.c. potassium hydroxide to 15 grms. of a 10 p.c. aqueous solution of thallous sulphate. The solution is filtered, cooled to −15°, and 3·5 grms. of a 3 p.c. solution of hydrogen peroxide is added with constant shaking. The oxide forms a bluish-black, lustrous precipitate, is readily decomposed into thallic oxide and thallous hydroxide by cold water and by dilute acids. It readily absorbs carbon dioxide, and, unlike thallous salts, is oxidised by a current of oxygen at ordinary temperature to thallic oxide (Rabe, Zeitsch. anorg. Chem. 1908, 58, 23).

.When a mixture of thallous sulphate and oxalic acid is electrolysed at the ordinary temperature with a current of 3–4 volts and 0·15–0·2 ampères, the oxide Tl_3O_5 or TlO_2,Tl_2O_3 is deposited on the anode. When the deposit is dissolved in dilute hydrochloric acid, chlorine is evolved and a yellow salt $TlCl_3,3TlCl$ is formed (Gallo and Cenni, Atti R. Accad. Lincei, 1908, [v.] 17, ii. 276).

For the halogen and mixed halogen compounds of thallium, *see* Wells and Penfield (Zeitsch. anorg. Chem. 1894, 6, 312); Meyer (*ibid.* 1900, 24, 321; *ibid.* 1902, 32, 72); Thomas (Compt. rend. 1900, 131, 892, 1208; *ibid.* 1901, 132, 80, 1487; *ibid.* 133, 735; *ibid.* 1902, 134, 545; *ibid.* 135, 1051; *ibid.* 1906, 142, 838; *ibid.* 143, 282; Ann. Chim. Phys. 1907, [viii.] 11, 204); Cushman (Amer. Chem. J. 1900, 24, 222; *ibid.* 1901, 26, 505); Maitland and Abegg (Zeitsch. anorg. Chem. 1906, 49, 341); Stolzenberg and Huth (Zeitsch. physikal. Chem. 1910, 71, 641). Thallium halides form double salts with many other metals (Meyer, *l.c.*; Thomas, *l.c.*; Pratt, Zeitsch. anorg. Chem. 1895, 9, 19; Wells and Foote, Amer. J. Sci. 1897, 3, 466; Ephraim and Heymann, Ber. 1909, 42, 4456; Ephraim and Barteczko, Zeitsch. anorg. Chem. 1909, 61, 238; Gewecke, Annalen, 1909, 366, 217; Delépine, Compt. rend. 1909, 149, 1072).

Thallic sulphide Tl_2S_3 is formed when the metal is fused with excess of sulphur. It is black and above 12° is plastic, but below 12° it is hard and brittle. When sulphuretted hydrogen is passed into a solution of a thallous salt, *thallous sulphide* Tl_2S is formed as a black precipitate, which can be obtained in a crystalline form (Staněk, Zeitsch. anorg. Chem. 1898, 17, 117; *see* also Loczka, Chem. Zentr. 1898, i. 657; Hamley, J. Amer. Chem. Soc. 1907, 29, 1011). According to Pélabon (Compt. rend. 1907, 145, 118) the sulphides Tl_8S_7, Tl_2S_5 also exist (*see* Hofmann and Höchtlen, Ber. 1903, 36, 3090). Double sulphides with copper and tin are also known (Bruner and Zawadski, Bull. Acad. Sci. Cracow, 1909, 312; Hawley, J. Phys. Chem. 1906, 10, 654).

Thallium sulphates and their double salts are described by Stortenbeker (Rec. trav. chim. 1902, 21, 87); Kohn (Zeitsch. anorg. Chem. 1908, 59, 111); Piccini and Fortini (*ibid.* 1902, 31, 451); Locke (Amer. Chem. J. 1902, 27, 280); Meyer and Goldschmidt (Ber. 1903, 36, 238).

Thallium sulphite is a white granular crystalline powder (Scubert and Elten, Zeitsch. anorg. Chem. 1892, 2, 434; *ibid.* 1893, 4, 44).

Thallium nitrates are described by Wells and Beardsley (Amer. Chem. J. 1901, 26, 257); Meyer (*l.c.*); Thomas (Compt. rend. 1904, 138, 1697); van Eyk (Zeitsch. physikal. Chem. 1905, 51, 721).

Thallium mercurous nitrate, m.p. 76°, sp.gr. 5·3°, gives a clear mobile liquid miscible with water and not reacting with sulphides. It forms a useful liquid for the separation of mineral sulphides (Retgers, Jahrb. Min. 1896, ii. 183).

Thallium nitrite forms double salts with cobalt and other metals (Przibylla, Zeitsch. anorg. Chem. 1898, 18, 448; Cunningham and Perkin, Chem. Soc. Trans. 1909, 1569; Tanatar and Petroff, J. Russ. Phys. Chem. Soc. 1910, 42, 94).

Thallium azoimide or *nitride* TlN_3 remains unchanged when heated to 340°, but explodes when heated more strongly or when struck (Curtius and Risson, J. pr. Chem. 1898, [ii.] 58, 261; also Dennis and Doan, J. Amer. Chem. Soc. 1896, 18, 970).

Thallium oxalate $HTl(CO_2)_4 3H_2O$ is prepared by treating the freshly precipitated hydroxide at 25° with a large excess of a cold saturated solution of oxalic acid. When suspended in absolute alcohol, cooled to 0°, and treated with dry ammonia, the compound $Tl(CO_2)_4NH_4(NH_3)_2$ is formed; at a higher temperature the compound $Tl(CO_2)_4NH_4$ separates. The pyridine salt $Tl(CO_2)_4HC_5H_5N$ and the salt $Tl(CO_2)_6(NH_4)_3$, as well as other oxalates $Tl(CO_2)_3(CO_2H)_2,3H_2O$ and $Tl_2(CO_2)_4,3H_2O$ have also been obtained (Rabe and Steinmetz, Ber. 1902, 35, 4447).

Thallous carbonate and *cyanide* are also known.

For a number of other thallium salts, *see* Stavenhagen, J. pr. Chem. 1895, [ii.] 51, 1; Giorgis, Gazz. chim. ital. 1894, 24, ii. 474; Joly, Compt. rend. 1894, 118, 649; Mauro, Real. Accad. Lincei, 1893, ii. 382; Hofmann, Zeitsch. anorg. Chem. 1896, 12, 55; Piccini, *ibid.* 1897, 13, 441; Piccini and Marino, *ibid.* 1901, 27, 62; Marino, *ibid.* 1909, 62, 173; Glauser, *ibid.* 1910, 66, 437; Dennis and Doan, *l.c.*; Wyrouboff, Bull. Franc. Min. 1896, 19, 219; Hawley, J. Amer. Chem. Soc. 1907, 29, 300; Kurowski, Ber. 1910, 43, 1078.

THALLOCHLORE. A name given by Knop and Schnedermann to the green colouring matter of lichens (Annalen, 56, 147).

THAPSIC ACID $C_{16}H_{30}O_4$. Obtained from the dried roots of *Thapsia garganica* (Linn.) (Canzoneri, Gazz. chim. ital. 13, 514; 24, ii. 437); m.p. 123°–124°. The anhydride melts at 71°.

THEBAINE *v.* VEGETO-ALKALOIDS.

THEINE or *Caffeine* *v.* VEGETO-ALKALOIDS.

THENARD'S BLUE. *Cobalt blue* *v.* PIGMENTS.

THENARDITE. A mineral consisting of anhydrous sodium sulphate (Na_2SO_4), crystallised in the orthorhombic system. It is found as large crystals, 6 ins. or more in length, on the shores of salt lakes in arid regions, and sometimes forms beds of considerable extent, together with glauberite, &c. Localities are: Borax Lake in San Bernardino Co., California; on the Rio Verde in Arizona; Rhodes Marsh in Nevada; Tarapaca and elsewhere in Chile; Espartinas near Madrid; and the salt lakes north of the Caspian. L. J. S.

THEOBROMA CACAO *v.* Cocoa.

THEOBROMIC ACID $C_{19}H_{39}COOH$ is obtained from cocoa butter and melts at 72°; it is apparently identical with arachidic acid (*q.v.*).

THEOBROMINE *v.* Vegeto-alkaloids.

THEOBROMOSE, THEOCIN, THEOLACTIN, THEOPHORIN, THEOPHYLLIN, *v.* Synthetic drugs.

THEOPHYLLINE *v.* Vegeto-alkaloids.

THERMIT PROCESS. 'In a thermit reaction a metallic compound (*e.g.* an oxide) is reduced by one or several metals or metallic alloys in such a way that when the mixture is ignited at one place, the reaction continues to go on spontaneously with complete oxidation of the reducing element, a fluid slag being formed, whilst the reduced metal is obtained as a compact uniform regulus; if the oxide is used in excess, the reduced metal is free, or practically free, from the element used as reducing agent' (H. Goldschmidt, Electrochem. and Metall. Ind. 1908, 6, 360).

In 1898 Goldschmidt (Stahl and Eisen, 1898, 18, 408; J. Soc. Chem. Ind. 1898, 17, 543, 584, 649; Zeitsch. für. Elektrochem. 1898, 4, 494; 1899, 6, 53) succeeded in reducing the oxides of chromium, manganese, iron, copper, titanium, boron, tungsten, molybdenum, nickel, cobalt, zirconium, vanadium, columbium, tantalum, cerium, thorium, barium, calcium, sodium, potassium, lead, and tin very conveniently by means of aluminium. Such reduction processes had been anticipated, owing to the fact that measured with respect to the same quantity of oxygen, aluminium has a greater heat of oxidation than almost any other metal. Earlier attempts to carry out such experiments had, however, proved very unsatisfactory; either the reactions would not begin, or they occurred with explosive violence. Goldschmidt overcame the difficulty by mixing the finely-divided oxide intimately with powdered or granulated aluminium, and starting the action at one point by raising its temperature sufficiently high. The reaction being once initiated, the enormous heat developed causes it to spread quickly throughout the entire mass, the time of reaction not varying appreciably with the quantity of material employed, and being about 30 seconds in the case of iron oxide and aluminium. To start the reaction at one spot, Goldschmidt placed a small heap of a mixture of powdered aluminium (or magnesium) and barium peroxide on top of the mixture to act as a fuse, and inserted therein a strip of magnesium ribbon. On lighting the latter, the fuse ignites, and the thermit reaction is started.

Owing to the heat developed in these reactions and the rapidity with which they occur, an enormous temperature is produced, second only to that of the electric arc. It has been estimated at 2600°–3000°, and direct observation with a Féry radiation pyrometer has shown that the temperature of a stream of steel produced from iron oxide and aluminium, as it was poured from the crucible, was 2300° (the melting-point of steel is approximately 1350°). At such temperatures the entire contents of the crucible remain liquid; the reduced metal sinks to the bottom, covered with a layer of molten alumina.

Other metals have been tried for the reduction of metallic oxides. Perkin (Faraday Soc. Trans. 1907, 3, 115, 179), and also Goldschmidt have tried calcium, but the reactions are too violent to be of much use, whilst the slag is difficultly fusible. Silicon (made in the electric furnace) has also been tried; but the reactions are too slow. The so-called mixed-metal, which consists essentially of cerium has, however, been successfully employed in the preparation of pure vanadium, columbium, and tantalum (Muthmann, Weiss, and Riedelbauch, Annalen, 1907, 355, 58; Weiss and Aichel, *ibid.* 1904, 337, 370).

A number of mixtures may be used in place of aluminium, and some have been patented. A mixture of equal parts of *calcium*-thermit and *silicon*-thermit, so that the active elements, calcium and silicon, are in the ratio of 2 to 1, is especially effective (Fr. Pat. 361197, 1905). It reacts like an ordinary aluminium-thermit, yielding a thin fluid slag having approximately the composition $4CaO{\cdot}3SiO_2$, and melting at 1425° (Boudouard, Iron and Steel, 1905, 352). The active mixture may be prepared either by mixing or alloying calcium with silicon (*v.* Fr. Pat. 388638, 1908). A mixture of *magnesium* and *silicon* may also be used to replace aluminium, giving a reaction like ordinary thermit (Eng. Pat. 3089, 1906; Fr. Pat. 364313, 1906; U.S. Pat. 902871, 1908), whilst magnesium itself acts similarly to calcium in its reactions with metallic oxides. *Magnesium-silicon* thermit is best mixed in proportions which yield a slag of the composition $7MgO{\cdot}4SiO_2$. A third mixture, viz. *aluminium*-thermit and *calcium*-thermit, gives very good results. The proportions may vary between wide limits, avoiding too large an excess of calcium, and the calcium aluminate slag is more fusible than alumina. A mixture containing 40 p.c. calcium-thermit produces a very fluid slag $3CaO{\cdot}2Al_2O_3$, and has a heat effect greater than that of aluminium-thermit (Fr. Pat. 361197, 1905; addn. Jan. 1906; U.S.A. Pats. 875345, 1907; 875666, 1907; 906009, 1908; Eng. Pat. 926, 1906). *See* also Watts and Breckenridge, Electrochem. & Metall. Ind. 1908, 6, 237; Weston and Ellis, Faraday Soc. Trans. 1907, 3, 170; 1908, 4, 60, 130; 1910, 6, 144; and Skinder, Chem. Zentr. 1909, i. 629.

Technical applications. Although the thermit reaction (Goldschmidt's reaction) only dates from 1898, it has acquired great technological importance, and the subject of 'aluminothermics' has been extensively developed.

Preparation of metals and alloys. The following are obtained by reducing the requisite metallic oxides (or mixtures of oxides) with a slight deficit of aluminium; chromium, manganese, molybdenum, ferro-titanium, ferro-vanadium, ferro-boron, manganese-copper, manganese zinc, manganese-tin, manganese-titanium, chromium-manganese. They are of great value in the iron and steel and other metallurgical industries; chromium, in particular, is largely employed in the manufacture of high-speed tool steel and armour plate. The metals and alloys produced are *carbon-free.* The crucibles in which the preparations are carried out must be lined with magnesia (Eng. Pat. 9610, 1905; Fr. Pat. 354597, 1905), one of the few oxides that aluminium is unable to reduce. The best method of procedure to ensure a maximum yield of chromium or manganese consists in mixing 1–4 p.c. of higher oxide with the bulk of lower oxide to be reduced to metal (Eng. Pat. 20004, 1905; Fr. Pat. 358071, 1905; U.S. Pat. 895628, 1908).

For experimental purposes, steel of any grade can be made by the thermit process, since the heat developed is sufficient to melt thoroughly small portions of even the most refractory metals. The thermit steel is free from carbon, but may be converted into high carbon steel by the addition of cast-iron shot.

The *slag* produced is also of commercial value. It may be employed in the preparation of aluminium, or used in place of natural corundum. It is especially valuable for use in the manufacture of pottery, for which purpose it is mixed with clay and burned (D. R. P. 160780, 1901). *Corubin*, an abrasive material for making emery wheels, emery cloth, &c., is prepared by crushing the slag obtained as by-product in the manufacture of chromium.

Welding iron and steel, and repairing broken steel castings. The advantages of the thermit process for these applications are that it is simple, rapid, requires no special skill, and enables repairs to be made *in situ*, when any other process would necessitate a dismantling of apparatus.

The mixture employed is composed of powdered aluminium and magnetic iron oxide, and when ignited yields half its weight of molten steel. Its registered trade name is 'thermit.' The reaction

$$8Al+3Fe_3O_4=4Al_2O_3+9Fe$$

indicates that approximately 3 parts of aluminium powder require 10 parts of magnetic oxide, and produce 7 parts of iron. Early literature on the subject gives the reaction as

$$2Al+Fe_2O_3=Al_2O_3+2Fe,$$

but examination of thermit with a magnet will show that the magnetic oxide is now employed. It is added in the form of granulated rolling-mill scale.

The firing of a charge of thermit produces a pure mild steel of the following average composition—

Carbon	0·05–0·10
Manganese . . .	0·08–0·10
Silicon	0·09–0·20
Sulphur	0·03–0·04
Phosphorus . . .	0·04–0·05
Aluminium . . .	0·07–0·18

Two methods of welding are in use, (*a*) the reaction serving merely as a source of heat (Eng. Pat. 18328, 1899), and (*b*) the steel produced by the reaction being utilised as well (Eng. Pat. 10859, 1901; 20894, 1900; U.S. Pat. 729573, 1903). In process (*a*) pure materials need not be used, and, if necessary, the thermit may be diluted with a cheap oxide, *e.g.* iron ore or sand, to lower the final temperature reached. This process is used in the butt-welding of pipes and bars. The ends are cut square, smoothed, and clamped together. A mould is then clamped round the junction. A charge of thermit is fired in an ordinary magnesia-lined crucible, allowed to stand half a minute so that slag and steel may separate (the volume of the molten slag is three times that of the iron produced), and then poured out so that the slag comes first. As the slag is poured in the mould on to the pipe, it forms a hard casing around the metal, and the liquid which follows distributes its heat uniformly through this casing to the metal. In about a minute the pipes have been raised to welding heat. The ends are then pressed tightly together by means of screws arranged in position beforehand. The mould is then removed, the slag collar carefully knocked off, and the red-hot joint allowed to cool. Process (*b*) has been largely employed in welding together tram and railway line sections. The ends are brought together and clamped accurately in position. A refractory clay mould is clamped round the ends and the requisite charge of thermit fired in a crucible placed over the pouring gate of the mould. At the end of the reaction, the crucible is tapped from the *bottom* (*see* Fig. 1), and the liquid steel flows into the mould, passes upwards from the bottom of the mould, surrounds the base and web of the rail, with which it fuses on account of its enormously high temperature, and on cooling makes a solid steel joint.

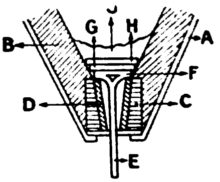
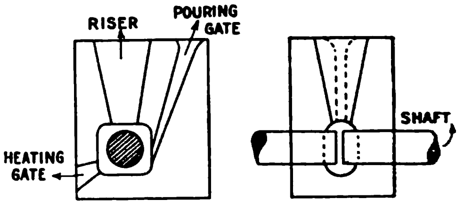


Fig. 1.—Tap-hole of Thermit Crucible.

A, iron casing; B, magnesia lining; C, hollow cylindrical magnesia stone; D, conical magnesia thimble; E, iron tapping pin, with flattened end F; G, asbestos washer; H, iron washer; J, layer of sand.

The welding of rails is a typical instance of the application of process (*b*) above, which is also employed for all kinds of repairing work, *e.g.* mending broken engine frames, driving rods and spokes, crank shafts, rudder and propeller shafts, stern-posts, &c., in fact, in the majority of cases where it is cheaper to repair than to replace. Where necessary, the fracture is opened out by drilling holes. A wax matrix is then built up over the break of the exact shape that the thermit steel collar to be fused into the casting is to have. Over this, in a sheet iron box, is constructed a mould, having a pouring gate, a preheating gate, and a large riser (Fig. 2). A gasoline torch, fed with compressed air, is then directed through the preheating gate. It melts out the wax, dries the mould, and heats the junction to be repaired to a bright red heat. Meanwhile, the crucible containing the thermit is arranged over the pouring gate. The quantity



Sectional views through mould

Fig. 2.

of thermit required is given by the rule: take 32 times the weight of the wax used, or 18 times as many ounces of thermit powder as there are cubic inches of surplus space in the mould. The crucible (Fig. 1) is designed so as to be tapped from the bottom (Goldschmidt, Zeitsch. Elektrochem. 1901, 7, 935; Cohn, J. Gasbeleucht. 1901, 44). The gasoline torch is withdrawn when the junction is red hot, the preheating gate plugged with a sand core held in readiness, and the thermit fired without delay. After the reaction is over, and the molten liquid has stood 30 seconds to allow the slag to rise, the crucible is tapped. The molten steel passes down the pouring gate, around the fractured joint, and up into the riser. The ends of the casting melt into the liquid steel, and on cooling, one homogeneous mass is formed. The projecting collar of thermit steel around the joint is left on whenever possible.

The average tensile strength of a thermit steel joint is about 30 tons per square inch cross-section. If the projecting collar of thermit steel has to be planed off, and the tenstile strength of the joint is less than that of the body of the casting, the weld may be made stronger by introducing *nickel* into the composition of the thermit; 1 p.c. of nickel increases the tensile strength of the weld about one-third. For a 1 p.c. alloy, 2 p.c. of nickel thermit may be added to the usual steel thermit, or 5 oz. of metallic nickel may be added to each 100 lbs. of thermit.

Thermit powder is supplied in 50 or 100 lbs. drums. For use in repair work, about 2 p.c. of manganese and 5 p.c. of mild steel punchings are added. The former acts as a purifier of the steel produced; the latter serves to lower the final temperature of the reaction and so prevent the contents of the crucible from boiling over.

Use of thermit in foundry practice. (*a*) The thermit reaction provides a ready means of introducing in an iron ladle a material which will stir up or pole the entire contents of the ladle, and at the same time produce an increase of temperature. For this purpose, the thermit is contained in cylindrical cans with a sleeve in the middle, suitable for passing on an iron rod. The can is held by the iron rod under the surface of the metal, where the reaction takes place. This procedure prevents the iron from becoming too dull to pour (U.S. Pat. 733957, 1903).

(*b*) A convenient means of purifying the iron in the ladle, by reducing the presence of harmful nitrogen in the molten metal, consists in holding a can of *titanium-thermit* under the surface as described in (*a*). This thermit is a mixture of pulverised aluminium and a titanium-iron oxide. The titanium set free in the reaction is sufficient to combine with the nitrogen in the ladle, titanium cyanonitride being produced. During this formation, the entire contents of the ladle are stirred up, to give the gases an opportunity of escaping. The iron is thereby rendered hotter and distinctly more fluid, and castings made from it are distinguished by their closeness of grain, being especially well adapted for withstanding pressure, *e.g.* cylinders, valves, &c.

(*c*) The enormous heat developed may be utilised to decrease the size of the risers of steel castings. The thermit, contained in suitable cans, is held in the neck of the riser, which is thus kept in the liquid state for a longer time than would otherwise be the case, thereby facilitating the proper feeding of the casting. The same principle is successfully applied to reduce the size of lost heads of steel ingots.

(*d*) In foundries where it is of importance to occasionally make a steel casting in a hurry, burning down the requisite quantity of thermit with an admixture of steel punchings affords by far the easiest method of procedure.

See also Hart's Welding (McGraw-Hill Book Co.).

THERMOFUGIN, THERMODIN, *v.* SYNTHETIC DRUGS.

THERMOMETERS. Changes of temperature are measured by the corresponding alterations produced in one or other of the physical properties of a substance. Thus the expansion of solids, liquids, and gases, the vapour pressures of liquids, the electrical resistance of metals, and other properties have been utilised for the determination of temperature.

In nearly every case the amount of change produced by a given rise or fall of temperature depends on the nature of the substance, and must therefore be carefully determined beforehand for the particular material employed.

There is, indeed, only one known method of measuring temperature which is theoretically perfect, that is to say, which is entirely independent of the nature of the substance; this method, proposed by Lord Kelvin, depends on the ratio of the work done by a reversible heat engine to the heat supplied to it, and the temperature, reckoned from absolute zero, may be defined as the reciprocal of Carnot's function. The method is not one, however, that is capable of practical application.

It has been found that within certain limits of temperature and pressure the expansion of all gases is very nearly the same for equal changes of temperature. Hence it is possible to devise a method of measuring temperature which, while practically independent of the nature of the (gaseous) substance employed, is at the same time fairly convenient for many purposes. It is important also to remark that the values given by an air or gas thermometer are in very close agreement with Lord Kelvin's thermo-dynamical temperatures.

The relation of the volume of a gas to its temperature and pressure may be stated simply as follows: The volume of a gas varies inversely as the pressure and directly as the absolute temperature, or $pv=c\text{T}$, where p is the pressure, v the volume, T the absolute temperature, and c a constant depending on the units chosen. If the volume remains constant the pressure varies directly as the absolute temperature, or $p=c'\text{T}$, while if the pressure is kept constant the volume varies directly as the absolute temperature, or $v=c''\text{T}$.

It is true that the co-efficients of expansion of different gases are not absolutely identical, and that the law holds good only within certain limits of temperature and pressure; but under pressures not greatly exceeding that of the atmosphere the deviations are extremely small in the case of nitrogen, hydrogen, helium, and some other gases, except at very low temperatures. Very accurate investigations of the properties of gases at extremely low temperatures have been carried out by Kamerlingh Onnes and his collaborators at Leiden, and their results show that the constant volume hydrogen thermometer gives nearly accurate results down to −250° and the helium thermometer to still lower temperatures.

An 'air' thermometer may be so constructed that (1) the pressure remains constant and the alteration of volume is measured; (2) the volume remains constant and the change of pressure is observed; (3) both pressure and volume are allowed to alter, and both are measured. The air or other gas is contained in a bulb of glass, or for very high temperatures of some other material, connected by means of a capillary tube with a mercury or sulphuric acid manometer. The bulb is heated to the required temperature while the other parts of the apparatus remain at the temperature of the room. If the pressure be kept constant the gas will expand, and at high temperatures a considerable portion of it will pass into the cold part of the apparatus and must be measured at the ordinary temperature; it is therefore usually considered better to raise the pressure so as to keep the volume of gas as nearly constant as possible. The vessel containing the gas expands, however, when the temperature rises, and a correction on account of this expansion must be introduced.

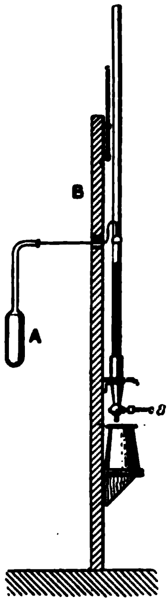


FIG. 1.

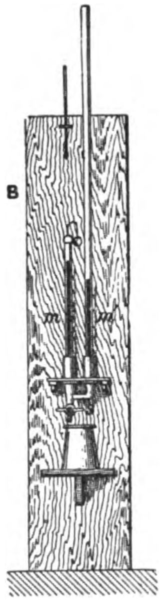


FIG. 2.

There are also three sources of error which are difficult to estimate, but they may be almost entirely eliminated by taking suitable precautions. The first depends on the fact that at ordinary temperatures air condenses to a slight extent as a sort of film on the surface of glass, while at high temperatures this condensed air is converted into gas, so that the apparent expansion is a little greater than the real. If, however, the bulb, after thorough exhaustion at a high temperature, is filled with air from which all moisture and carbon dioxide have been removed, the error becomes practically negligible (Callendar, Phil. Trans. 178A, 161).

The second is due to slight changes of volume which a glass vessel is liable to undergo after being strongly heated and allowed to cool again. The magnitude of the possible error becomes extremely small, however, if the bulb is heated for some hours to at least the highest temperature which is to be registered, before its volume is determined. This point will be more fully discussed when dealing with mercurial thermometers. The third source of error is due to the deformation of the bulb or to leakage of gas through it when the temperature and the internal gaseous pressure are greatly raised. This difficulty has been overcome by Day and Clement (Amer. J. Sci. 26, 1908), who employed a platinum-iridium bulb containing nitrogen, by surrounding the bulb with nitrogen at the same pressure as that within the bulb.

Of the numerous forms of air thermometer which have been devised, the three shown in the diagrams may serve as examples. The first (Fig. 1) represents a form of instrument employed by Regnault in his classical researches. The bulb A of the thermometer is connected by a capillary tube (passing through a perforation in the screen B) with the mercury manometer *mm'*, a front view of which is shown in Fig. 2. By addition of mercury to the open limb *m'*, or by its removal by means of the stopcock *s*, the mercury in the limb of the manometer connected with the air thermometer may be always kept at the same height, so that there is no alteration of the volume of air except that due to the expansion of the bulb when heated.

The calculation of the temperature is based on the fact that the mass of air remains constant, although its temperature, its pressure, and, to a small extent, its volume undergo change. Let

V=volume of bulb A at 0°;

v=volume of capillary tube, together with the small portion of the manometer above the mercury in m, also at 0°;

α=coefficient of increase of pressure of dry air at constant volume;

κ=coefficient of expansion of glass;

D=mass of 1 c.c. of air at 0° and 76 cms. pressure;

P=observed pressure—that is to say, the barometric pressure, *plus* or *minus* the difference of level of the mercury in m and m'.

When the bulb is placed in melting ice, while the capillary tube and manometer are at the temperature t° of the room, the total mass of air will be

$$D.P.\left\{V+\frac{v(1+\kappa t)}{1+\alpha t}\right\}$$

When the bulb is heated to the unknown temperature x, the temperature of the capillary tube and manometer being now t', the mass of air will be

$$D.P.'\left\{\frac{V(1+\kappa x)}{1+\alpha x}+\frac{v(1+\kappa t')}{1+\alpha t'}\right\}$$

Therefore

$$P\left\{V+\frac{v(1+\kappa t)}{1+\alpha t}\right\}=P'\left\{\frac{V(1+\kappa x)}{1+\alpha x}+\frac{v(1+\kappa t')}{1+\alpha t'}\right\}$$

an equation in which everything is known but x.

Values of α for several gases for the temperature range 0° to 100° are given below, p_0 being the initial pressure (at 0°).

	p_0	a
Hydrogen	760 mm.	0·0036627
Helium	700 „	0·0036626
Nitrogen	760 „	0·0036714
Oxygen	663 „	0·003674

If the volume of air be allowed to vary, the limb *m* of the manometer must be graduated, and should be surrounded by cold water of known temperature. In this case the additional volume *v′* at the temperature of the water must be brought into the equation.

Sulphuric acid may be employed with advantage in place of mercury, since it moves more freely in a narrow tube, and, being lighter, allows of more delicate readings; or a small sulphuric acid gauge may be interposed between the thermometer and the mercury manometer. An apparatus which can be employed either as a constant volume or constant pressure manometer has been described by Callendar (*l.c.*) and more fully by Callendar and Griffiths (Phil. Trans. 182A, 119). It is represented in Fig. 3.

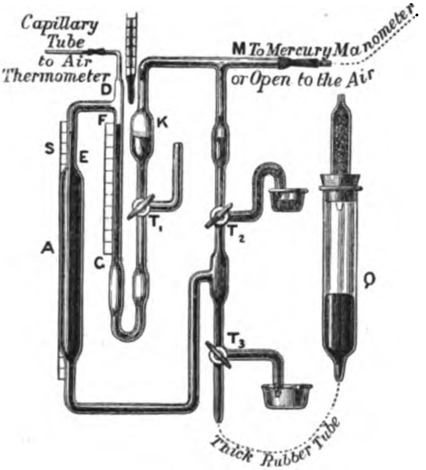


FIG. 3.

When the measurement is to be made at constant volume the mercury in A is brought up to the zero point, and the stopcocks T_2 and T_3 are closed. The level of the sulphuric acid in the gauge is then regulated by means of an ordinary mercury manometer, not shown in the diagram, and the pressure is the algebraical sum of the barometric pressure, that registered by the mercury manometer, and the slight difference in level, if any, of the sulphuric acid in the two limbs of the gauge FK, divided by the specific gravity of mercury compared with that of sulphuric acid.

If the pressure is to be kept constant, the tube A is first filled from the reservoir Q until the level of the mercury stands at some point in the tube DE, recorded by the scale S, the pressure of the air in the bulb being equal to that of the atmosphere, as shown by the sulphuric acid gauge. (In this case the tube M is not connected with the mercury manometer, but is open to the air.) When the bulb is heated, mercury is allowed to escape by the three-way tap T_2 into the weighed beaker, the tap being closed as soon as the sulphuric acid gauge indicates that the pressure is again equal to that of the atmosphere. The increased volume is calculated from the weight of mercury expelled. The narrow tubes DE and FG are calibrated and provided with scales. For the advantages of the sulphuric acid gauge see also Bottomley (Phil. Mag. 1888 (Aug.), 149).

Callendar has (Nature, 1891, 45, 212) described a modified constant-pressure air thermometer which appears to possess marked advantages over those previously devised, and gives extremely accurate results. The pressure of the air in the thermometer is not adjusted to equality with that of the atmosphere, but always with the same constant pressure, obtained by connecting the outer limb of the sulphuric acid gauge to a glass bulb filled with air and kept in melting ice.

The effect of changes of temperature of the connecting tubes on the readings is entirely eliminated by the employment of compensating tubes of the same size, and thus the troublesome and somewhat uncertain correction hitherto necessary is obviated. The compensation is perfect when (1) the two sets of connecting tubes are of equal volume and at the same mean temperature; (2) the mass of air inclosed in the standard pressure-bulb is equal to that in the thermometric and mercury bulbs; (3) the pressures are adjusted to equality. Under these conditions, the temperature of the thermometer bulb (on the air-thermometer scale) is given by the simple equation $\theta_1 = V_1\theta_0/(V_0 - Vm)$, where V_1 is the volume of air in the thermometer bulb at θ_1°, V_0 and Vm are the volumes of air at 0° in the standard pressure bulb and the mercury reservoir (this being also surrounded by melting ice), and θ_0 is the temperature of melting ice on the air-thermometer scale.

For moderate ranges of temperature, and when extreme accuracy is not required, the apparatus may be greatly simplified, and may be so constructed that the temperatures are read directly on the sulphuric acid gauge; it is stated that such thermometers can be made to read to the tenth of a degree at 450°. This form of direct reading thermometer has been patented and is recommended for technical purposes.

Other forms of air thermometer have been described by Balfour Stewart, Phil. Trans. 153, 425; Codazza, Dingl. poly. J. 210, 255; Jolly, Pogg. Jubelband, p. 82; Mitscherlich, Annalen, 12, 146; Crafts, Ann. Chim. Phys. [v.] 14, 409; Andrews, Ber. 14, 2116; Pettersson, J. pr. Chem. [ii.] 25, 102; Cailletet, Compt. rend. 106, 1055; Berthelot, Ann. Chim. Phys. [iv.] 13, 144; Murray, J. Phys. Chem. 1897, 1, 714. A platinum bulb was recommended by Pouillet (Compt. rend. 3, 782), but it was pointed out by Becquerel (Ann. Chim. Phys. 58, 49) that at high temperatures air passes through the platinum. A porcelain bulb was employed by Weinhold (Pogg. Ann. 149, 188), by Deville and Troost (Ann. Chim. Phys. [iii.] 58, 265), and others. According to Holborn and Day (Wied. Ann. 68, 817; Amer. J. Sci. 8, 165; 10, 171), however, porcelain does not give satisfactory results at high temperatures. They recommend bulbs of Jena boro-silicate glass, No. 59^{III}, containing hydrogen for temperatures up to 500°, and bulbs of a platinum-iridium alloy (10 p.c. Ir) with pure nitrogen gas from 500° to 1300°. The

Pt-Ir bulbs should be heated electrically or else protected from gaseous combustion products, which are liable to pass through the alloy. Day and Sosman (Amer. J. Sci. 1910, 29) have measured temperatures up to 1550°. Harker proposes to make bulbs of rare earths such as those used for Nernst filaments.

For very low temperatures, the glass bulbs should contain hydrogen or helium. A very complete account of the hydrogen thermometer in use at the cryogenic laboratory at Leiden is given by Kammerlingh Onnes and Clay (Communication No. 95*e*).

As regards the theory of the subject and the comparison of the temperatures registered by different gas thermometers with each other and with the thermodynamical scale, reference may be made to the following memoirs and papers: D. Berthelot, Sur les thermomètres à gaz, Paris, 1903; Ann. d. poids et mesures, 1907, 13*b*, 3; Chappuis, Phil. Mag. 50, 433, 1900; 3, 243, 1902; Phil. Trans. 1900, 194, 37, 131,; J. Phys. 1904, 3, 833; Ann. d. poids et mes. 1907 13*a*, 3; Kammerlingh Onnes, Comm. 97*a* and *b*, 102*b* and *d*; Holborn, Ann. Physik. 1901, [vi.] 2, 242; Buckingham, Bureau of Standards, 1907, 3, 237; Phil. Mag. 1908, 15, 526; Rose-Innes, *ibid.* 1908, 14, 301.

Air thermometers for technical purposes are generally provided with scales which are calibrated empirically by heating the bulbs to two or three known temperatures, so as to obtain a certain number of fixed points. The scales are then constructed by interpolation.

Thermometers of this class have been described by P. Schoop, D. R. P. 20345, 1882; Witz, Compt. rend. 91, 164; Beilby, J. Soc. Chem. Ind. 1885, 41; Coleman, *ibid.* 1885, 43; Heisch and Folkard, and by Bristol (Mech. Eng. 1900, 6, 916). They consist of a porcelain bulb, a copper capillary, and a pressure gauge constructed with two spiral tubes on the Bourdon principle. They can be constructed as recording instruments. The thermometer of Heisch and Folkard is very simple, and has been found by Hurter (J. Soc. Chem. Ind. 1886, 635) to give good results. The bulb A (Fig. 4) contains air under reduced pressure, and there is a vacuum over the mercury in the manometer M.

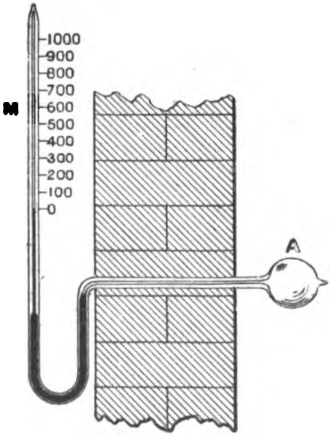


FIG. 4.

The mercurial thermometer. For ordinary purposes the mercurial thermometer is the most convenient, for it may be made of any required size, is easily portable, and the bulb, if elongated, need not be wider or, indeed, so wide as the stem. The instrument consists of a spherical or cylindrical bulb fused to a capillary tube of suitable length. The bulb is filled with pure mercury, which must be boiled for some time to remove the film of gas or aqueous vapour which adheres obstinately to the surface of the glass. If the thermometer is required for low temperatures only, there is usually a vacuum in the stem of the thermometer, but for high temperatures it is necessary, and for temperatures above 70° or 80° advisable, to fill the capillary tube with nitrogen to prevent distillation of the mercury, a small bulb being blown at the upper end of the tube in order that when the mercury expands and compresses the nitrogen the pressure shall not rise too high.

An ordinary thermometer is graduated by placing it *first* in the steam from water boiling under known pressure and then in melting ice (*v.* Guillaume, Traité pratique de la Thermomètrie de Précision, p. 112). The variation of the melting-point of ice with the pressure is so minute that this point may be taken as absolutely fixed, but the boiling-point of water varies considerably with the pressure, and therefore some standard pressure must be chosen. This is 760 mm. or 29·922 ins. of mercury measured at 0°C. and at the latitude of Paris for the Centigrade scale, and 29·905 ins. of mercury at 32°F. at the latitude of London for the Fahrenheit scale.

The position of the mercury in the stem is marked off a these two temperatures, and the space between these two fixed points is then usually divided into a certain number of equal parts—100 on the Centigrade scale, 180 on the Fahrenheit, and 80 on the Réaumur. On the Centigrade and Réaumur scales, the melting-point of ice is taken as the zero point, but on the Fahrenheit the zero of the scale is placed 32 divisions lower down, so that the melting-point of ice is 32°, and the boiling-point of water 212°.

A thermometer graduated in this manner does not, however, register true temperatures except at the two fixed points, for the following reasons:—1. It is impossible to obtain an absolutely cylindrical capillary tube, so that the volume corresponding to a scale division is not quite the same in all parts of the tube. Various methods have been devised for calibrating the stem (*v.* Brit. Assoc. Report, 1882, 145–204, also Guillaume, *l.c.* 43–99), but when this is done there remain other sources of error. 2. The position of the mercury in the stem at any temperature depends on the expansion both of the mercury and of the glass, and in each case the rate of expansion increases with rise of temperature. Moreover, different kinds of glass have different rates of expansion, so that two thermometers made of different materials—even if the capillary tubes were perfectly cylindrical—would give different readings at the same temperature. The only really satisfactory method of correction of such a thermometer is to compare its readings either directly with an air thermometer, or with another mercurial thermometer which has previously been standardised by means of an air thermometer. Or a series of fixed points may be determined by immersing the thermometer in a number of freezing liquids (melting solids) or by heating it with the vapours of a series of pure liquids boiling under known pressures. The following table contains a list of suitable substances with their melting-points, transition-points, or boiling-points, and the variation of pressure corresponding to 1° at the boiling-points, temperatures outside the range of the mercurial thermometer being included for convenience :—

Temperature	Fixed point
—183·0°	b.p. of oxygen ; $dp/dt=75{\cdot}9$ mm. per degree.
—158·0	m.p. of *iso*pentane.
—116·8	m.p. of ethyl ether.
—94·5	m.p. of toluene.
—63·3	m.p. of chloroform.
—38·7	m.p. of mercury.
—22·9	m.p. of carbon tetrachloride.
0	m.p. of ice.
32·38	tr.p. of sodium sulphate.
46·2	b.p. of carbon disulphide ; $dp/dt=24{\cdot}8$.
50·67	tr.p. of sodium bromide.
78·3	b.p. of ethyl alcohol ; $dp/dt=30{\cdot}5$.
100·0	b.p. of water ; $dp/dt=27{\cdot}1$.
132·0	b.p. of chlorobenzene ; $dp/dt=20{\cdot}2$.
156·2	b.p. of bromobenzene ; $dp/dt=19{\cdot}4$.
184·1	b.p. of aniline ; $dp/dt=19{\cdot}6$.
218·0	b.p. of naphthalene ; $dp/dt=17{\cdot}2$.
231·9	m.p. of tin.
305·8	b.p. of benzophenone ; $dp/dt=15{\cdot}8$.
321·0	m p. of cadmium.
356·7	b.p. of mercury ; $dp/dt=13{\cdot}3$.
419·3	m.p. of zinc.
444·5	b.p. of sulphur ; $dp/dt=11{\cdot}1$.
630·7	m.p. of antimony.
756·0	b.p. of cadmium ; $dp/dt=8{\cdot}1$ (calculated).
916·0	b.p. of zinc ; $dp/dt=7{\cdot}0$ (calculated).
960·9	m.p. of silver.
1083	m.p. of copper.
1452±2	m.p. of nickel.
1549±2	m.p. of palladium.
1755±5	m.p. of platinum.
2910	m.p. (approx.) of tantalum.
3080	m.p. (approx.) of tungsten.

For additional fixed points between 0° and —160°, *v.* Timmermans, Sci. Proc. Roy. Dubl. Soc. 1912.

In this way a table or curve of corrections may be constructed showing the error at any scale reading of the thermometer. 'Normal' thermometers may now be purchased ; they are compared with a standard thermometer before graduation, and nearly true temperatures are registered by them ; or the thermometers may be sent to the National Physical Laboratory, the Reichsanstalt, or the Bureau of Standards, and the necessary table of corrections obtained.

Tables of correction of readings of mercurial thermometers to true air-thermometer temperatures have been published by various observers ; but as these tables must necessarily vary for different kinds of glass—the further correction for unevenness of bore being also required—they do not seem to possess much *general* value. It may be useful, however, to give references :—Rudberg, Annalen, 36, 121 ; Bosscha, Compt. rend. 69, 875, 1185 ; Regnault, *ibid.* 69, 879, and Mémoires, 21, 239 ; Crafts, *ibid.* 95, 836 ; Recknagel, Pogg. Ann. 123 ; Guillaume, Traité pratique de la Thermométrie de Précision.

Even when the above corrections to true air-thermometer temperatures have been made, there remain some sources of error, the most important of which is the alteration of the capacity of the bulb, and doubtless also of the capillary tube after long-continued heating, and, indeed, after any considerable change of temperature. A vast amount of experimental work has been done on this subject, and the explanation of the observed changes has given rise to a great deal of discussion. The following references may be made to the literature of the subject :—Despretz, Compt. rend. 4, 926 ; Person, *ibid.* 19, 1314 ; Legrand, *ibid.* 4, 173 ; Crafts, *ibid.* 91, 291, 370, 413 ; 94, 1298 ; Pernet, *ibid.* 91, 471 ; E. J. Mills, T. Ed. 29, Part 2, 587, and Nature, 41, 100, 227, 538 ; Young, *ibid.* 41, 152, 271, 488 ; Tomlinson, *ibid.* 41, 198 ; Pernet, Travaux et Mém. du Bureau Int. des Poids et Mesures, i., B. 52, and I., 17 ; Guillaume, Traité pratique ; Marchis, Zeitsch. physikal. Chem. 1899, 29, 1 ; 1901, 37, 553, 605. The most important facts regarding the alteration of zero point may be shortly described as follows :—

1. If a thermometer be graduated shortly after the bulb has been blown, the zero point will rise with comparative rapidity at first, then more and more slowly, and the elevation of the zero point may go on for many years. Joule (Scientific Papers, i. 558) took observations with one thermometer over a course of thirty-eight years, and the change, which then amounted to almost exactly 1°F., was still proceeding.

2. If a thermometer be maintained at a high temperature for a considerable time, the rise of the zero point takes place with much greater rapidity, and so far as is known the higher the temperature the more rapid is the rise, and *apparently* the higher is the final point reached. A total elevation of over 20° in the case of German soda glass has in several cases been observed, while larger glass bulbs, after continuous heating to 445°, or in one case 511°, have been found by Regnault, Crafts, and Callendar and Griffiths to suffer a contraction of from 0·25 to 0·34 per cent. In all cases the rise or contraction, which is rapid at first, becomes slower and slower, and it seems doubtful whether at any given temperature actual constancy of zero point or capacity has ever yet been attained. If, however, a thermometer has been heated for many hours to a given high temperature and then allowed to cool very slowly, subsequent heating to lower temperatures has very little effect on the zero point, and it is advisable to subject a thermometer to this process before determining the fixed points. According to Marchis (*l.c.*), a fluctuating high temperature is more effective than a steady one in raising the zero point. Hecker (Zeitsch. f. Instrumentenkunde, Beib. 1901, 5, 41) describes a method of electrical heating and slow cooling. Böttcher (*ibid.* Beib. 1903, 17, 154) states that the thermometer bulb

should be heated for a short time to a temperature 100° above the initial softening temperature of the glass, and that slow cooling is unnecessary. The question is discussed by Dickinson (Bureau of Standards, 1906, 2, 189) and methods of treatment are recommended.

3. Not only is the zero point liable to change, but the interval between the zero and 100° points may at the same time be increased, for the coefficient of expansion of glass suffers diminution after prolonged heating.

4. Internal or external gaseous pressure on the bulb appears to have little or no influence on the rise of zero point.

5. If a thermometer—even after its zero point has been rendered as permanent as possible—be heated and then cooled very rapidly, a fall of the zero point will be observed, but after a day or two the greater part of this fall will be recovered, and the remainder after a longer period. The alteration of the zero point depends greatly on the nature of the glass, and a special hard glass is used by Tonnelot of Paris, while Schott and Co. in Germany employ two kinds of glass, 'normal thermometer' glass, 16^{III}, and a boro-silicate glass, 59^{III}, for the best thermometers. The latter glass is now generally used; it has a very high melting-point and can be used up to 550°, the mercury being prevented from boiling by the introduction of carbon dioxide under pressure (*cf.* Murrie, J. Soc. Chem. Ind. 1885, 45, 189, 655).

Other possible sources of error are the following:—If the mercury in the stem of the thermometer—or a portion of it—is not heated to the same temperature as that in the bulb, a correction is required, *v.* DISTILLATION. In order to ascertain the mean temperature of the unheated column, Guillaume (Compt. rend. 1891, 112, 87) places a supplementary thermometer without a bulb at the side of the thermometer stem. Modifications of this method have been proposed by Mahlke, Zeitsch. Instr. 1893, 13, 58; 1894, 14, 73; and by Adam, *ibid.* 1907, 27, 101.

The bulb is slightly compressible, and considerable changes of external pressure affect the readings to some extent.

Mercury does not move very freely in a capillary tube, and in delicate thermometers, when the temperature changes, the movement of the mercury may take place in jerks instead of smoothly. This may be avoided by tapping the thermometer (Pickering, Phil. Mag. 1886, 21). Greater freedom of motion is attained (Duclaux and Hamelin, J. Phys. 1910, 9, 600) by placing dilute sulphuric acid over the mercury, and electro-capillary effects are prevented by means of a recess full of mercury at the upper end of the capillary, the mercury in recess and bulb being connected by a platinum wire. The increase in sensitiveness was found to be so great that variations in the melting-point of ice with moderate change of pressure were readily observed.

For temperatures below the freezing-point of mercury, −38·7°, various liquids have been suggested to take the place of that metal. Alcohol and toluene thermometers have been in use for many years, and more recently, pentane has been found specially suitable for very low temperatures (Kohlrausch, Wied. Ann. 1897, 60, 463; Baudin, Compt. rend. 1901, 133, 1207; Rothe, Zeitsch. Instr. 1902, 22, 192; Hoffmann and Rothe, *ibid.* 1907, 27, 265). Baudin and Rothe recommend 'technical' in preference to pure pentane on account of its lower freezing-point. The b.p. is 25° to 33°, and the pentane thermometer can be used between 30° and −190°.

The molecular weight of a dissolved substance is very frequently calculated from the depression of the freezing-point or the rise of the boiling-point of a solvent. Thermometers of small range but great sensitiveness have been devised for these determinations by Beckmann, and a full description of various forms of the instrument is given by him (Zeitsch. Chem. 1905, 51, 329). The bulb is of large size and the same thermometer can be used for different temperature ranges by transferring part of the mercury from the bulb to a receptacle at the other end of the capillary. The value of a scale division is thereby slightly altered, and the necessary corrections are discussed and a table is given by Grützmacher (Zeitsch. Instr. 1896, 16, 171, 200).

Useful general information about mercurial thermometers is contained in the following papers: Chree (Phil. Mag. 1898, 45, 205, 299; Kohlrausch (Zeitsch. Instr. 1898, 18, 76); Scheel, *ibid.* Beib. 1899, 9–13).

Platinum resistance thermometers. The measurement of temperature by the alteration of the resistance to electricity of a platinum wire was suggested by Siemens (Bakerian Lecture, Proc. Roy. Soc. 1871), but in consequence of an adverse report to the British Association in 1874 this method was abandoned. Subsequently, however, the subject was investigated by Callendar, Phil. Trans. 1887, 178 A, 161; Phil. Mag. 1891, 32, 104; 1899, 47, 191; Griffiths, Phil. Trans. 182 A, 43, and both authors, *ibid.* 182 A, 119, with very satisfactory results. In order to insure accuracy the platinum wire must be pure in the first place; it must be prevented from alloying with silicon, carbon, tin, or other impurities, and it must not be subjected to strain—such as elongation. When these conditions were fulfilled, the resistance of a wire was always found to be constant at a given temperature. The form of thermometer recommended by Callendar and Griffiths is shown in Fig. 5. Two platinum wires are inter-wound in a double-screw thread, passing through holes in a thin mica plate AB. Each spiral is provided with a double and single electrode, symmetrically arranged. The six electrodes are insulated, and kept in place by passing through holes in thin mica wads (one of which is shown at C) which are cut to fit the glass tube containing the thermometer. The electrodes are best made of platinum, the ends of the wires being fused to them by the oxyhydrogen flame.

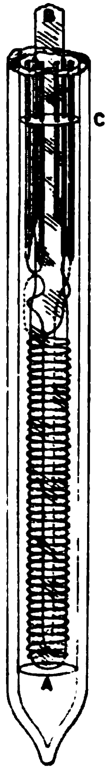


FIG. 5.

If R_0 and R_1 be the resistance at 0° and 100°, and R that at any other temperature, the corresponding value of the 'platinum' temperature *pt* is deduced by the formula

$$pt = 100\ (R - R_0)/(R_1 - R_0).$$

To reduce the platinum resistance temperature to that of the air thermometer the following formula is employed

$$T - pt = \delta\left[\left(\frac{T}{100}\right)^2 - \frac{T}{100}\right]$$

the value of δ, generally 1·5, depending on the wire and being determined for each thermometer from observations at 0°, 100°, and 444·5°. The formula has been found to hold up to 1000° or 1100°. To avoid errors due to variation of the room temperature, compensating leads are used, and other improvements have been adopted from time to time. For further details *v.* PYROMETRY.

For moderate temperatures, nickel is recommended in place of platinum by Marvin (Phys. Rev. 1910, 30, 522).

Dewar (Proc. Roy. Soc. 1904, 73, 244) states that platinum does not give good results at very low temperatures and recommends gold or silver. Meilink also (K. Akad. Wet. Amsterdam, 1904, 13, 212, 221) obtained better results with gold than with platinum. The resistance of gold, platinum, and other metals at low temperatures has been accurately determined by Kamerlingh Onnes and Clay, Comm. 99*c* and 107*c*.

Comparisons of the platinum scale of temperature with the hydrogen, nitrogen, or air scale have been carried out by Harker and Chappuis (Phil. Trans. 1900, 194, 37) at Sevres; Meilink (K. Adak. Wet. Amst. 1902, 10, 495); Holborn (Ann. Physik. 1901, [vi.] 2, 242); Harker (Proc. Roy. Soc. 1904, 73, 217); Travers and Gwyer, *ibid.* 1905, 74, 528), and Kamerlingh Onnes and Clay, *l.c.*, and of the platinum, gold, and hydrogen thermometers by Kamerlingh Onnes and Clay, Comm. 95*c*, *d*, and *e*; *v.* also Timmermans, *l.c.*

Thermo-electric thermometers. The first attempt to employ a thermo-couple for the measurement of high temperatures was made by Becquerel in 1826, but he failed to obtain concordant results. In 1886, however, Le Chatelier devised an instrument which gave good results and came into practical use, and since then great improvements have been introduced.

The thermo-electric thermometer consists essentially of two fine wires of different metals or alloys, fused together at one end, and connected through a galvanometer at their other ends, the fused end being placed in the source of heat. An E.M.F. is developed, which is roughly proportional to the difference in temperature of the two ends of the couple. Le Chatelier employed wires of Pt and Pt·Rh (10 p.c of Rh), and this couple may be used up to 1600°. The other couples which have been employed most frequently are Pt and Pt·Ir (10 p.c. Ir), and Cu and constantan (a Cu-Ni alloy with 40 p.c. Ni); the former may be used for temperatures as high as 1200°, the latter up to 500°. For full account of these thermometers *v.* PYROMETRY.

A great variety of couples have been tried for both high and low temperatures. For high temperatures the couples mentioned have been found to give the best results, but the Pt·Ir alloy has the disadvantage that the Ir volatilises, very slowly even at 900°, and much more rapidly at 1200°. For low temperatures, Holborn and Wien (Wied Ann. 1896, 59, 213) have recommended Fe—constantan; Pellat (Compt. rend. 1901, 133, 921), Fe—Zn; Dewar (Proc. Roy. Soc. 1905, 76, 316); Pt—German silver; whilst Kamerlingh Onnes and Clay (Comm. 107*b*), find that Ag—Au gives the best results. At about −256° this couple is about twice as sensitive as one of constantan—steel.

Comparisons of the thermo-electric scale of temperature with the air or hydrogen scale have been made by Holborn and Wien (Wied. Ann. 1895, 55, 95; 1896, 59, 213); Harker (Proc. Roy. Soc. 1904, 73, 217); and at low temperatures (−59° to −259°) by Kamerlingh Onnes and Crommelin, Comm. 95*a*; and with the platinum resistance scale by Waidner and Burgess, Bureau of Standards, Bull. 1909, 6, 149.

The question of the calculation of the true temperature of the hot junction when the cold one is not at 0° has been fully discussed by Offenhaus and Fischer, Electrochem. Ind., New York, 6, 1908, 362.

Vapour pressure thermometer. This form of instrument was recommended by Lord Kelvin (Pr. E. 1880, 432), and was introduced into practice under the name of the 'Thalpotassimeter' by Schäffer and Budenberg (Dittmar, J. Soc. Chem. Ind. 1885, 44). If the vapour pressures of a given liquid have been accurately determined through a certain range of temperature, any temperature within these limits may be afterwards determined by observing the pressure exerted by the vapour of the liquid.

The method possesses the great advantage that alteration of the capacity of the vessel containing the liquid and vapour is entirely without influence on the pressure, which is solely dependent on the temperature.

Probably the most serious objection to the method is the difficulty of filling the vessel or reservoir with the pure liquid *entirely free from air*, and if this difficulty be not overcome large errors may be introduced. For high temperatures, a mercury vapour pressure thermometer is sometimes serviceable (Ramsay and Young, Chem. Soc. Trans. 47, 651). The mercury must be well boiled to remove the film of air adhering to the glass, but this may be done without much difficulty. A liquid oxygen vapour pressure thermometer is recommended for temperatures between −183° and −200° by Stock and Nielson, Ber. 1906, 13, 39, 2066, and excellent results have been obtained with such an instrument by Kammerlingh Onnes and Braak, K. Akad. Wet. Amsterdam, 1908, 11, 333. Vapour pressure thermometers and pyrometers have been devised by Fournier, and an account of these instruments is given by Marieni (Electricità, Milan, 1908, 30, 82).

The following papers or memoirs on the subject of thermometry may be consulted: Sur les thermomètres à gaz, D. Berthelot, Paris, 1903; Kohlrausch, Zeitsch. Instr. 1898, 18, 16; Guillaume, Thèrmomètrie de précision; Chree, Phil. Mag. 1898, 45, 205, 299; Scheel, Zeitsch. Instr. 1899; Callendar, Nature, 1899, 59, 494, 519; Phil. Mag. 1899, 47, 191; Barus, Int. Phys. Congress, Paris, Rep. 1, 1900, 148.

S. Y.

THERMONATRITE *v.* NATRON; TRONA.

THERMOSTATS. A thermostat may be defined to be an apparatus so arranged as to maintain the temperature of a space constant between certain definite limits. Previous to 1860, the forms of apparatus employed were comparatively few and simple, but during the last half century the refinement of physical and chemical experimental methods has led to the design of very numerous varieties of thermostats. Some few of these have been adapted to technical uses; in general these applications present little complexity and do not call for any detailed description. They have mainly been applied to the temperature regulation of steam and gas heating systems and more recently to the control of electrical heating. Among other purposes the temperature control of incubators heated by gas or electricity, of acetylene heated germinating stoves, and of pasteurising apparatus used in the sterilisation of milk are noteworthy. The automatic regulation of the temperature of fermenting worts, of dye-vats, of evaporating pans and vacuum stills, has resulted in improvements in the sugar, spirit, and dyeing industries. Similarly, thermo-regulators are extensively adapted to secure the more exact and economical working of lacquering, brazing, tempering, annealing, and roasting ovens and kilns. Numerous systems for the central heating of public buildings and houses by steam, hot water, gas, and hot air are now automatically regulated by thermometric or electrical control apparatus. Similar thermostatic arrangements are also used in connection with steam-heating devices in railway carriages. In gas-testing stations, rooms are maintained at a uniform temperature by thermostats controlling the gas-heating system. Automatic fire-alarm devices are usually supplied with thermometric or electrical thermostats arranged to give warning by telegraphic or mechanical signals.

The thermostats and thermo-regulators suggested may be classified as:—

I. Thermostats depending on a flow of heated liquid for the maintenance of a constant temperature.

II. Thermostats utilising the latent heat of the alteration of the state of aggregation or change of phase of a body:

(*a*) Change of phase at freezing-point or cryohydric-point.
(*b*) Change of phase at boiling-point.
(*c*) Change of phase at inversion-point.

III. Other thermostats not automatically regulated through mechanical or electrical means.

IV. Self-regulating thermostats, including—

(*a*) Mercurial or other single-liquid thermometers:
  1. Acting directly on the gas supply or other heat source;
  2. Acting on the source of heat through electrical arrangements;
  3. Acting on the source of heat through mechanical arrangements;
(*b*) Gas thermometers:
  1. Acting on the gas supply by transmission of pressure through a liquid column;
  2. Acting through electrical arrangements;
  3. Acting through mechanical arrangements;
(*c*) Vapour-tension thermometers:
  1. Air and vapour;
  2. Vapour in contact with its own liquid only;
(*d*) Thermostats depending on the differential expansion of solid substances;
(*e*) Electrically heated thermostats with electrical control;
(*f*) Other mechanical regulators.

The limits of this article preclude the description of more than a few of the more typical examples of each of these classes; details of other forms and references may be obtained from: Temperature Regulators, J. T. Brown; Laspeyres, Pogg. Ann. 152, 132; H. Hammerl, Carl's Rep. 18, 1882; K. Arndt, Zeitsch. Chem. Apparatenkunde I. 255–263; Fr. Grützmacher, Zeitsch. Instrumentenkunde, 22, 184, 193, 201; W. C. Geer, J. Phys. Chem. 6, 85–105, 1902, who gives a general discussion and a useful bibliography; M. Bodenstein, Zeitsch. physikal. Chem. 1899, 30, 113–139, who supplies a detailed account of thermostats used in gas-reaction researches, and H. W. Fischer and O. Bobertag, Zeitsch. Elektrochem. 1908, 14, 375

I. *Thermostats depending on a flow of heated or cooled liquid for the maintenance of a constant temperature.* The form of apparatus invented by C. Blaufus-Weiss may be adapted for use either as a pressure or temperature regulator (D. R. P. 43574, 1887). As used in the latter capacity, it consists essentially of a cylindrical valve controlling the supply of hot or cold currents of either liquid or vapour to a worm arranged in the vat to be maintained at a uniform temperature. The valve is formed by an elliptical slit in a sheet cylinder which passes half round the circumference of the cylinder, and, when the latter revolves, is brought more or less opposite to tubes opening into the sides of the drum, which serves as a valve-box. The space within the revolving cylinder is furnished with tubes passing through the head of the drum to serve as supply or exit pipes. The valve is worked by the rise and fall of a vertical piston, actuated by the expansion and contraction of a quantity of mercury, which is contained in a bell-shaped vessel of which the wider end is applied to a small chamber which forms a side continuation of the vat. The vertical movement of the piston is transformed into the circular motion of the valve in a horizontal plane by means of a pin working in a screw slot on a hollow cylinder.

A simple thermostat for use in connection with the refractometric examination of oils and fats, by T. E. Thorpe (Chem. Soc. Trans. 1904, 257), uses a constant current of liquid, under a defined pressure head, heated by passing through a coil in the vapour of a boiling liquid (*v.* vol. iv. 555).

W. Behrens (Zeitsch. Wiss. Mikrosk. 1895, 12, 1) describes a neat air-worked expansion valve for controlling a hot-water current supplied to the hot stage of a microscope.

Other forms using this principle are given by J. Ph. Grünig, D. R. P. 75882, 1893; J. C. Schalkwijk, Zeitsch. Inst. 1901, 21, 338; and T. M. Lowry, Trans. Faraday Soc. 1907, 3, 119.

II. *Thermostats utilising the latent heat of the alteration of the state of aggregation or change of phase of a body.* (*a*) References to types using the change of phase at the freezing-point and cryohydric point will be found in Geer's bibliography (*l.c.*). To these may be added Travers (Zeitsch. physikal. Chem. 1905, 52, 443), using alcohol and carbon dioxide snow for low temperatures.

(*b*) The change of phase at the boiling-point is more generally utilised. The vapour from a liquid boiling at the required temperature is caused to surround the oven or bath to be heated. Here the temperature will vary according to the pressure under which the liquid is boiled.

The liquids used for this purpose are:—Water, ether, methyl and ethyl alcohols, benzene, toluene, acetic acid, carbon disulphide, amyl alcohol, xylene, turpentine, aniline, naphthalene, glycerol, diphenylamine, the monohydrate of sulphuric acid, mercury, paraffin, sulphur, zinc.

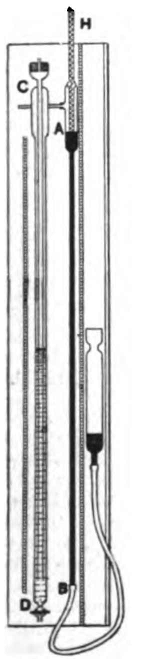


Fig. 1.

The temperatures so obtained lie between 22° and 1040°. At the ordinary atmospheric pressure one definite temperature is obtained for each substance used. Intermediate temperatures may be obtained in several ways:—(1) The pressure under which the vapour is formed is varied; (2) mixtures of liquids in various proportions are used; (3) a solid is dissolved in a liquid, the boiling-point being thus raised, and the vessel or bath is surrounded by the boiling liquid.

L. Meyer devised an apparatus for determining the boiling-point of a liquid at any pressure below that of one atmosphere. It may be used to control a constant-temperature bath (Annalen, 15, 303). The apparatus (see Fig. 1) is a pressure control valve. The mercury in AB cuts off the connection with the air-pump through H as soon as the pressure is reduced to the required point; CD is a mercury valve which admits air to the apparatus immediately the pressure falls below that fixed upon.

Brown has improved this apparatus, rendering it possible to use it for pressures higher, as well as lower, than one atmosphere. A mercury manometer is so constructed that, immediately the pressure falls below or rises above that determined upon, an electro-magnetic clutch, actuating a suitable stopcock, is placed in a battery circuit, and thus connection is made between the reservoir and the pump or outer air, as may be required for adjustment (Phil. Mag. 1879 [v.] 7, 411).

A. Fock has constructed a very serviceable bath, in which common petroleum is used as the mixture of liquids of different boiling-points. A double cylinder AB (Fig. 2), serving as a vapour-jacketed bath, is connected by means of the side tubes *a* and *b* with the reflux condenser G. The tube C connected with the condenser communicates, through the stopcock *r* and tube *d*, with the reservoir flask K. A mixture of liquids (*e.g.* common petroleum) is placed in the bath and distilled, the distillate passing through the open stopcock *r* into the flask K. At the moment when the required temperature is attained, as indicated by the thermometer T, the stopcock *r* is closed; the distillate now returns through the tube *b* to the bath, hence the temperature of B will remain constant for any length of time (Ber. 1885, 18, 1124).

Ramsay has used a vapour-bath in which the temperature is controlled by regulating the pressure under which a selected pure liquid is boiled (Chem. Soc. Trans. 1885, 640).

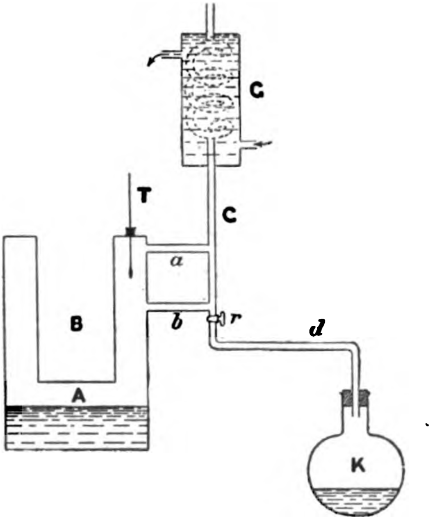


Fig. 2.

J. Traube and L. Pincussohn (Zeitsch. Inst. Beib. 1897, 17, 49) have also devised a simple thermostat using a boiling liquid under a controlled pressure. For other forms *see* Geer (*l.c.*).

(*c*) Richards and Churchill (Zeitsch. physikal. Chem., 1898, 28, 313) have similarly used the change at inversion points.

III. *Other thermostats not automatically regulated.* Instruments serving as indicators only have been devised by Hall (Q. J. Sci. 1818, 5, 52); Doyère (Ann. Chim. Phys. 1850, [iii.] 28, 5); A. Fraser (Jour. Gas Lighting, 1881, 38, 798); J. Barnes (Chem. Soc. Trans. 1881, 39, 463); A. V. Harcourt (Proc. Roy. Soc. 1882, 34, 166); U. Kreusler (Chem. Zeit. 8, 1321); and C. Winkler (Ber., 1885, 18. 2533).

Bunsen's thermostat (Annalen, 141, 273) is historically interesting.

Exner's thermostat is of especial value, as it allows of constant temperatures being maintained between 0° and 10° (see Fig. 3). It consists of an inner flask, surrounded by two concentric glass vessels, with an air space between the three vessels are fastened above to a zinc plate. A delicate thermometer and a thermo-element are placed in the centre of the flask; the stem and wires pass through a leaden pipe attached to the zinc plate. Between the two surrounding vessels is coiled a German-silver wire, the coils hanging freely without contact with either vessel; wires pass from the coil to a battery through the leaden tube. The whole is completely immersed in melting ice, contained in a fourth vessel; the leaden tube alone projects, and serves to keep the wires from contact with the ice. By passing an electric current through the German-silver coil, the temperature of the central vessel can be maintained at any desired point above 0° (Sitz. W. 1873, 68, 2).

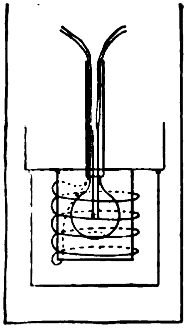


FIG. 3.

The same principle is applied by H. Crew (Phil. Mag. [v.] 33, 89). The accompanying illustration (Fig. 4) shows the points in which this instrument differs from the preceding one. Julien storage cells are used as the source of a constant current, which is regulated by alteration of the length of a resistance wire through which the current flows, by means of a slider and controlled by means of a Thomson balance.

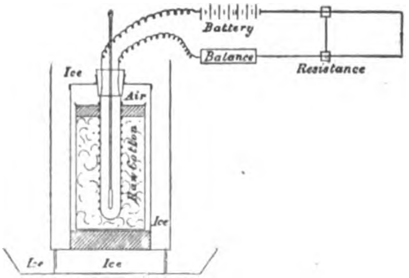


FIG. 4.

Other non-automatic instruments are described by Mahlke (Zeitsch. Inst. 1893, 13, 197), Pulfrich (Zeit. Inst. 1898, 18, 49), and Rothe (*ibid.* 143. 1899, 19).

IV. *Self-regulating thermostats*: (a) *Single-liquid thermometers* (1) *acting directly on the gas supply or other heat source.* Thermostats of this and allied types have been frequently utilised in connection with technical processes and heating systems; references to a number of these are given at the end of this article.

Reichert's form of regulator is essentially that of a mercury thermometer, with a reservoir at the top of the column. The gas-supply tube is placed so that its contracted opening is vertically over and near to the surface of the top of the mercury column. The leading tube takes off gas at the side of the reservoir. A small side tube on the stem is supplied with a screw by means of which the mercury level may at any time be adjusted, and the temperature maintained thus altered at will (Fig. 5) (Zeitsch. anal. Chem. 11, 34; Pogg. Ann. 144, 467).

Gerhardt's modification permits the instrument to be filled easily with mercury.

Regulators of the same type, but varying somewhat in form, have been constructed by Page (Chem. Soc. Trans. 1876, 24), Fletcher (*ibid.* 1876, 488), and Roulin (Dingl. poly. J. 227, 263). The instrument devised by Roulin is made of iron and steel (*v.* Fig. 6). The height of the mercury column is adjusted by means of a sliding tempered-steel rod, held in position by the set screw *f*. As this rod passes down the centre of the gas-supply tube, the gas can only reach the burner tube by passing through the ring-shaped aperture *d*, near the surface of the mercury. A small tap *g* maintains a sufficient supply of gas to the burner to avoid extinction of the flame by the complete interruption of the supply at *d*.

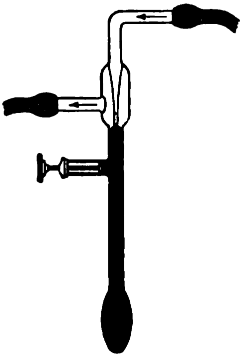


FIG. 5.

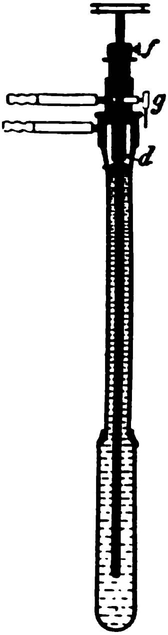


FIG. 6.

In the thermostatic battery by Dibdin and Smith, in use at the metropolitan gas stations, large mercurial thermometers are employed. The tubes by which they communicate with the supply tube are provided with stopcocks, so that any one or more of them may be thrown out of action. They control the gas supply to the boiler connected with the hot-water pipes.

For more accurate work, the mercury has been replaced by 30 p.c. calcium chloride solution, alcohol, benzoline, petroleum, xylene, or toluene. The toluene regulator has gained general acceptance: a simple and easily constructed form, designed by H. Lunden and W. Tate (Zeitsch. Chem. Apparat. II. 1, 13, 1907), is shown in the sketch (Fig. 7) with dimensions in millimetres. The column of calcium chloride solution prevents contact of the toluene with the mercury and with the stopcock R, thus doing away with the slow evaporation of the expanding liquid and allowing the use of ordinary lubricants with the stopcock provided to make temperature adjustments. This regulator, without the aid of any form of pressure regulator (the gas pressure varying from 50 to 60 mm. of water), maintained the temperature of a water-bath of 150 litres capacity during 30 days constant in a room varying considerably in temperature. The greatest difference between the extreme temperatures (observed at regular and frequent intervals) was 0·02°. A small part of the heating gas only passed through the valve D, sufficient to heat the bath within a short interval of the required temperature was supplied direct from the main.

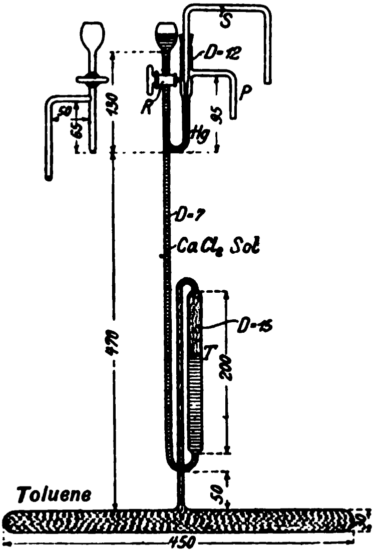


Fig. 7.

Another convenient form of toluene regulator is described by Lowry (J. Soc. Chem. Ind. 1905, 1033): there is a helical toluene reservoir tube coiled round a straight vertical stem containing mercury; it is provided with a wide bye-pass but has no provision for ready adjustment of the temperature, and the mercury and toluene are in contact near the lower end of the helix.

Hannay (Mon. Sci. [iii.] 16, 1021) and F. W. Dafert (Chem. Zeit. 1886, 52, 789) have designed thermostats belonging to this class. Further references are given by Geer (J. Phys. Chem. 1902, 6, 85).

(2) *Thermostats acting on the source of heat through electrical arrangements.* The usual type of this class employs a mercury thermometer with one pole of a battery permanently connected with the mercury and a second adjustable pole which completes the circuit at the desired maximum temperature. An electromagnetic arrangement in the circuit actuates a gas-cock, or works a gas valve either directly, or, by means of a plunger, indirectly controls a mercury valve of the usual type. This form of thermostat can be made very rapid in action and practically independent of variations in the gas pressure.

Scheibler has constructed an electro-thermostat, with the usual form of electric thermometer (Fig. 8). The electro-magnet is contained in the square box A; the upper end of the armature is provided with a leather pad, which works against the continuation of the gas-supply tube *b*, and with it forms a valve which cuts off the gas when the mercury comes into contact with the upper platinum wire. The extinction of the flame is avoided by having a small hole at *c* in the tube *b*, more or less closed by means of the screw *d*, through which a small stream of gas can escape into the box, and hence into the burner tube (Zeitsch. Anal. Chem. 1868, 88).

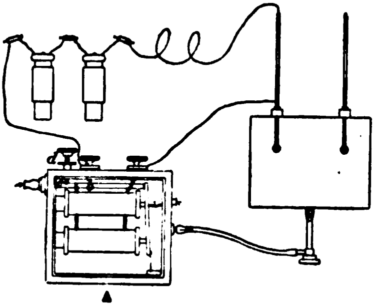


Fig. 8.

Kohlrausch adapted this principle to the regulation of the temperature of a hothouse (Dingl. poly. J. 389, 175). E. E. Reid (Amer. Chem. J. 1909, 41, 148–152) employs a mercury valve worked by a plunger controlled by an electromagnet.

Other forms are quoted by Geer (see iv. 1); to these we may add Clerget (Dingl. poly. J. 134, 23), Pfaundler (Carl's Rep. 18, 443), and Salet (Bull. Soc. chim. 1865).

(3) *Thermostats acting on the source of heat through mechanical arrangements.* Randall's apparatus (Dingl. poly. J. 224, 478) admits of direct technical applications, as it is adapted to the heating of large masses of water to a constant temperature by the use of steam. In Fig. 9 *b* is a thin-walled tubular vessel containing some expansible liquid, the movements of the surface of which are followed by the piston K. This piston works a valve *v*, which controls the steam supply. The spring *f* insures the return of the piston, the movements of which are recorded by the indicator I, which thus acts as a thermometer.

D'Arsonval constructed a very delicate thermostat (Fig. 10) by surrounding his oven with a chamber completely filled with water, which is introduced through an opening *v*, closed by a screw or by a cork through which a thermometer passes. Connected with this water chamber is the side tube O, closed by a caoutchouc membrane. Near to the centre of the surface of the membrane the gas-supply tube terminates, in a small metallic valve-box, from which the gas is led off to the burner by the tube *d*. The expansion or contraction of the large volume of water

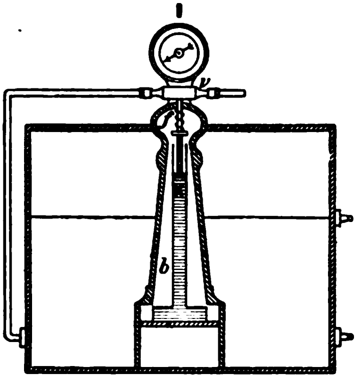


FIG. 9.

in the outer chamber causes the caoutchouc membrane to lessen or increase the distance between the supply tube and its own surface, thus forming a very sensitive valve, which controls the supply of gas to the burner. This regulator is said to keep the temperature constant to $\frac{1}{200}$° (J. Pharm. Chim. [iv.] 26, 474).

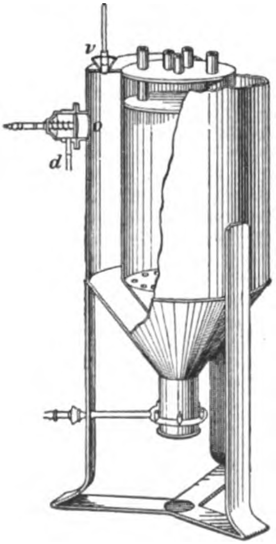


FIG. 10.

To maintain constant higher temperatures than can be employed with water, D'Arsonval substitutes a brass tube (Fig. 11), containing petroleum or glycerol, for the surrounding water chamber. The membrane is replaced by a corrugated metallic plate such as would be used in an aneroid barometer; *b* is a leaden tube prolonging the brass tube; it is hermetically closed after charging the tube. The chamber at the back of the aneroid plate communicates with the main tube by two small tubes *m* and *n*.

Several other forms of this regulator, retaining the same kind of valve, have been constructed. The valve itself has been mounted separately on a stand, and provided with a funnel and stop-cock to adjust the amount of liquid in the connected reservoir and the lower part of the valve, and with a bye-pass to insure that the flame be never quite extinguished. The same type of valve has also been adapted to the regulation of the flow of a cooling mixture, used for obtaining temperatures below that of the surrounding air.

G. Dorian (Bull. Soc. Ind. Mulhouse, 1900. 71, 249) described a combined heat and moisture regulator, in which the expansion of the liquid of a thermometer with a reservoir of spirally twisted tube controls a cock regulating the current of heating fluid and a hydrometer regulator works the moisture supply. T. S. Patterson (J. Soc. Chem. Ind. 1902, 21, 456), N. A. Randolph (Jour. Franklin Institute, 1883, 116, 465), V. H. Veley (Chem. Soc. Trans. 43, 370), and Nauman (Dingl. poly. J. 226, 276), give other forms, and various technical adaptations will be found in the list given at the end of this article.

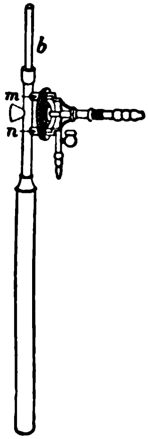


FIG. 11.

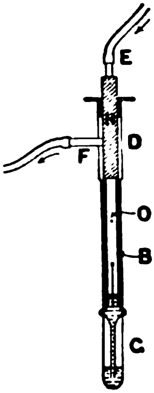


FIG. 12.

(*b*) *Gas thermometer regulators.*

(1) *Acting on the gas supply through a liquid piston.* A thermostat on this principle was devised by Kemp (Dingl. poly. J. 117, 352) and improved by Westly.

Bunsen's thermostat is a modification of Kemp's. The gas supply and exit tubes are arranged as shown in Fig. 12; the supply tube E passes through a brass cylinder H, which screws into the loose brass cap D. At its lower end is a slit, and it is provided with a minute orifice at O; the exit tube F is joined on to the side of the cylinder H, the latter being continued by the glass tube B to the same depth as the supply tube. The cap is fitted on a brass tube supplied with a slit in which the tube F can slide. A glass cylinder closed at the lower end continues this brass tube. In the lower part of this glass vessel is a glass air-chamber opening downwards and closed by the mercury contained in the cylinder; this air-chamber preferably takes the form shown at G. The expansion of air in the chamber causes the mercury to rise in the cylinder, and thus partially closes the slit; the position of the slit is regulated by the screw cap until the required temperature is attained. The minute orifice O insures that the gas supply should never be completely cut off (Dingl. poly. J. 143, 342).

Bunsen's low-temperature regulator has a larger air chamber, and is provided with a side tube and stopcock, by means of which the amount of mercury present can be readily altered (Desaga's Catalogue). Pontallie divides the gas supply after passage through a Bunsen's regulator, using one part to heat the regulator only, the remainder heating the bath. As these quantities are in exact and determined proportion, the temperature of the bath is maintained constant when that of the regulator does not vary.

Schorer separates the air-thermometer reservoir from the valve to enable the instrument to be used for high temperatures (Zeitsch. anal. Chem. 9, 213).

D'Arsonval adapted his thermostat for use at temperatures between 150° and 1200° by substituting an air reservoir for the petroleum reservoir employed at lower temperatures. The reservoir was made of glass or porcelain. The aneroid valve was at the same time furnished with a lever-arm and weight P, by means of which the pressure on the lower surface of the aneroid plate could be more or less compensated, and the amount of gas supplied altered at will (Fig. 13) (J. Pharm. Chim. [iv.] 26, 474).

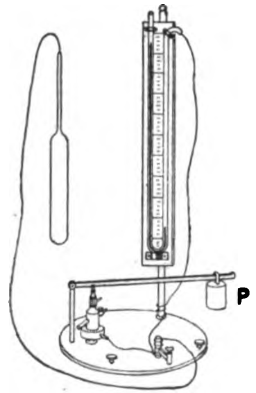


FIG. 13.

Although a number of varieties of this type have been used (*see* Geer's bibliography; J. Martenson, Chem. Zentr. 1872, 513; Clowes, Chem. Soc. Trans. 24, 639; L. Saarbach, J. Amer. Chem. Soc. 18, 511, 1901), and the principle has been technically applied in connection with furnaces of moderately high temperature, for low temperature work the toluene thermometer forms are to be preferred for accurate long period temperature regulation; all gas and vapour thermostats suffer from the defect of needing regulation with the changes in pressure of the air.

(2) *Acting through electrical arrangements.* These devices resemble the instruments in group iv. *a* (2). Pfaundler's apparatus (Carl's Rep. 18, 443) is similar to Scheibler's, the points of difference are sufficiently evident from the annexed figure (Fig. 14).

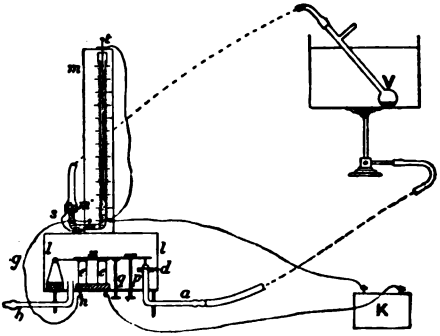


FIG. 14.

(3) *Acting through mechanical arrangements.* Jeannel's thermostat (Fig. 15) is an air-thermometer thermostat in which the air reservoir consists of a metallic vessel of 300–400 c.c. capacity. This is connected with one limb of a U-tube containing glycerol. In the other limb a float G carries a steel needle working loosely in a fine caoutchouc tube O. By a rise of the liquid in F, the float, guided by the steel needle, brings the flat upper surface of the sealing-wax H, in which the needle is mounted, near to the mouth of the tube O, thus forming a valve controlling the current of gas from the supply tube J to the exit tube P, of which O is a continuation. The pressure of the air in A is modified at pleasure by means of the caoutchouc pump S, with which connection is made through the tap R on a side tube (Ann. Chim. Phys. [iv.] 25, 386).

W. T. Richmond (Amer. Chem. J. 5, 287), Bendix and Lohse (D. R. P. 1880, 14242; Ber. 14, 2608), and Bechem (D. R. P. 1881, 18077; Ber. 15, 1226) have also devised self-acting thermo-regulators of this type.

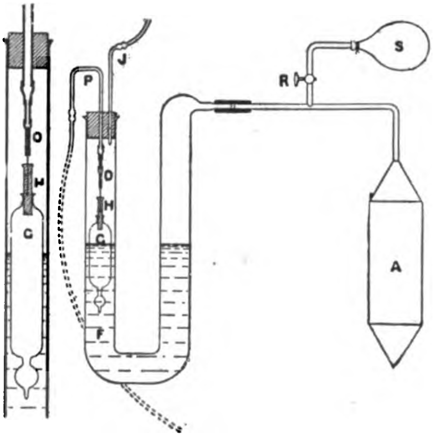


FIG. 15.

(*c*) *Vapour-tension thermometers.*

(1) *Air and vapour.* Andreæ's thermo-regulator is a Kemp thermostat in which the expansion of the air in the reservoir is increased by the addition of a small quantity of some readily

volatile liquid. Such liquids as ether, alcohol, acetone, light petroleum and water may be employed for the purpose. Ether is particularly suitable, on account of the rapid increase of its vapour tension with increase of temperature. A thermostat of this form will maintain the temperature of a water-bath constant within 0·04–0·05° (Wied. Ann. 4, 614).

Lothar Meyer has also made use of the same principle (Ber. 16, 1088).

Benoit's thermo-regulator has the thermometer reservoir separated from the valve, connection being made by means of a caoutchouc tube containing mercury.

The reservoir consists of a thin tube, drawn out at one end for convenience in filling, which contains a small quantity of air, and a few drops of some volatile liquid; the remainder of the space in the tube is occupied by mercury in connection with the mercury in the valve by means of the caoutchouc tube. The valve differs somewhat from the ordinary form. It is provided with a side tube A (Fig. 16), by which a small amount of gas can directly pass from the supply tube x to the burner tube y. Mercury can be added by means of the side tube B, or withdrawn from the cock C to adjust the level within the valve. The whole is mounted upon a sliding board, fixed by the clamp-screw M, at any convenient height (Wied. Beibl. 4, 296; Guillaume's Thermométrie, 130).

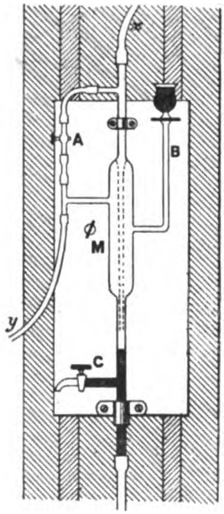


Fig. 16.

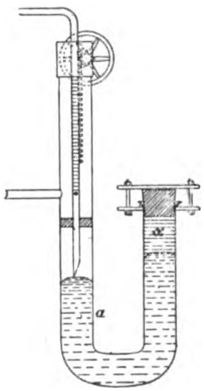


Fig. 17.

(2) *Vapour in contact with its own liquid only.* The instrument devised in 1886 by G. W. A. Kahlbaum belongs to this class. There is the usual mercury valve, the supply tube being bevelled off at the open end at an angle, and having a small hole opposite the exit tube to provide against total extinction of the flame. It may be adjusted according to the temperature required by the rack and pinion shown (Fig. 17). The other limb of the U-tube contains a liquid of boiling-point just below the temperature required in the bath or oven. For facility in changing the liquid, this end of the tube is closed by a tightly-fitting cork held in place by a clamp working against an india-rubber seat fixed on the collar of the glass tube.

The temperature rises just above the boiling-point of the liquid x, a portion of this volatilises, and mercury is forced up the limb a; the pressure on the liquid being now greater, its boiling-point is raised, and the temperature must increase for further volatilisation to occur. Owing to the rise of mercury in a, the gas supply is diminished, and hence the temperature falls. Consequent on the fall of temperature, a portion of the vapour condenses, the valve is opened to a greater extent, and the temperature again rises. These actions soon reach a point of equilibrium, and a constant temperature is then maintained (Ber. 19, 2860).

(*d*) *Thermostats depending upon the differential expansion of solid bodies.* Bonnemain (Dingl. poly. J. 16, 285) and Ure (*ibid.* 42, 173) devised regulators depending upon the expansion of simple or compound metallic bars.

Hipp's thermostat is only available for temperatures between 30° and 40° (see Fig. 18). It consists of a copper vessel K, surmounted by a wooden box C, having glass front and back. A system of tubes on the walls of the oven communicate with the vessel K, and serve for the circulation of the water heated in that vessel. They are provided with openings for filling in water, and to serve as escape vents in case the water may be accidentally boiled. The temperature is controlled by a regulator consisting of a bent compound metallic bar fixed upon the back wall of the oven at A; the free end B is connected by a copper wire with the lever h working a conical valve v; z is a regulating screw, by means of which any desired initial opening of the valve may be obtained; s is the gas-supply tube, and t draws off gas for the burner from the valve-box R (Dingl. poly. J. 191, 366).

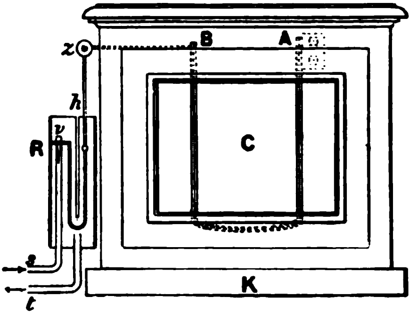


Fig. 18.

Lothar Meyer in 1884 devised a sensitive temperature regulator on this principle (Fig. 19). It consists of a long brass tube placed vertically in the bath, and closed at its lower extremity: in this tube a slightly longer glass rod is placed. The tube supports a rod carrying a movable lever-arm A, from which depends a floating valve B. The valve may be placed at varying distances along the lever-arm A, so that the difference between the expansions of the brass tube and glass rod may be magnified to a greater or less extent in the amount of movement imparted to the valve. The supply tube is a narrow-bore tube passing up the arm x of the valve working in the glycerol seal tube *m*. The supply tube and seal may be adjusted to any required height. A precisely similar arrangement allows of the drawing off through *o* of the gas for the burner. The valve *z* is essentially a Bunsen mercury-and-slit-tube valve. The mercury vessel is adjustable to any required height (Ber. 17, 478).

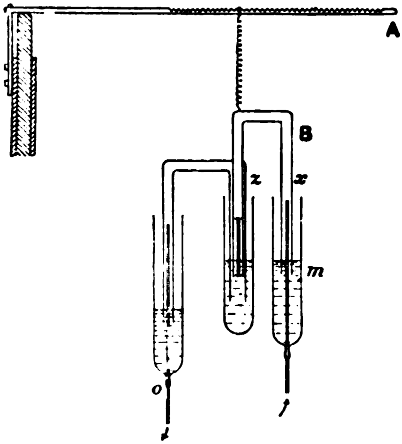


Fig. 19.

L. von Babo arranged a gas regulator, in which the control valve depends for its action upon the unequal expansion of glass and copper. In Fig. 20, A is a copper tube, B a glass rod. The valve x, which regulates the flow of gas from the supply G to the burner tube E, is fixed in position by the glass rod B, against which it is pressed by a spiral spring C. The screw D serves to adjust the position of the glass rod, and renders it possible to obtain a greater or smaller supply of gas at will. As the temperature rises, the expansion of the copper tube being greater than that of the glass rod, the valve x is pressed by the spring C nearer to its seat, and so there is less gas supplied; the temperature then falls, and the valve partially re-opens, and so on (Ber. 13, 1221).

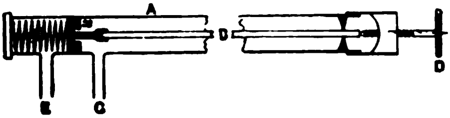


Fig. 20.

Kohlrausch employed a Breguet's metallic thermometer to make and break an electric current, which heated a fine platinum wire (Pogg. Ann. 125, 626).

E. Gumlich (Zeitsch. Inst. 1898, 18, 317) claims, by the use of a nickel and brass Brequet's spiral governing the gas supply through intermediary electrical arrangements, to have maintained a dry oven within 0·4° for long intervals.

Rieth's instrument consisted of a compound metallic bar working a cone valve. supplied with a regulator screw (Chem. Zentr. 1871, 615).

(*e*) ***Electrically heated thermostats with electrical control.*** Thermostats of this type allow of more sensitive and rapid adjustment than any other; they are particularly suitable for accurate scientific work but are not without technical applications.

Rothe (Zeitsch. Inst. 1899, 19, 143) gives a very complete account (with illustrations) of a thermostat designed for use in thermometer work at the Phys. Tech., Reichsanstalt. The same author (Zeitsch. Inst. 1902, 22, 14) adapts this principle to the construction of an instrument for use with very low temperatures. A Dewar's vessel serves to prevent conduction of heat from without; the heating coil is of constantan wire wound on the ebonite ring of a stirrer, the stem of which is of glass tubing through which pass the leading wires for the current.

W. C. Geer (J. Phys. Chem. 1902, 6, 94) claims for his thermostat a variation of 0·002° only for a 9 hours' run with a 30-litre bath. A somewhat simpler form, which is essentially a modified Geer thermostat, is described by F. A. Osborn (*ibid.* 1905, 9, 297). The accompanying diagram (Fig. 21) shows its essential features. The heating of the 50-litre bath is accomplished by means of an iron wire CC carrying a current from the large storage battery B. The wire forms a layer of five turns against the sides of the bath, which latter is encased in a non-conducting layer of felt. E is a glass worm, 9·5 cm. diameter and 16 cm. long and holding 110 c.c. of mercury, serving as reservoir of a regulating thermometer with a capillary stem. The bath is stirred by a mechanically-driven stirrer represented by D. A platinum fused-in wire permanently connects an electro-magnet R with the mercury of the thermometer. R is connected through a storage cell B′ with a second adjustable wire P. When the required temperature is reached, the mercury completes the circuit with P and the main current is broken at AA by the movement of the armature. The spring shown establishes the main circuit as soon as the mercury breaks contact with P.

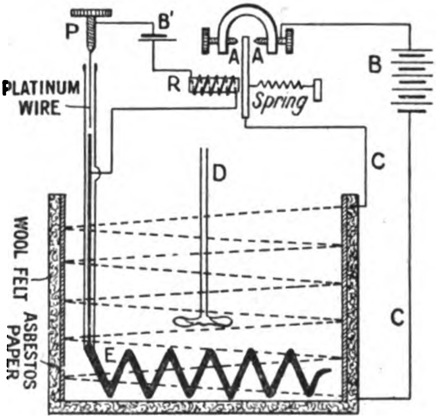


Fig. 21.

This form can be brought to the required steady temperature in 15 minutes and shows no change of a hundredth of a degree in 8 hours.

Other forms are given by S. W. Young (J. Amer. Chem. Soc. 1901, 23, 327); C. Marie and R. Marquis (Compt. rend. 1903, 136, 614), who use an acetone thermometer with mercury make and break and current through platinum wire; R. A. Macumber and C. G. L. Wolf (J. Path. Bact. 1904, 10, 105); H. Darwin (Phil. Mag. [vi.] 7, 408, 1904); J. P. Magnusson (J. Phys. Chem. 1907, 11, 25); Regaud and Fouilland (Ann. Chim. anal. 1909, 14, 141); L. Kolowrat (J. Phys. 1909, 8, 495), who describes the automatic regulation of an electric oven.

(*f*) *Other mechanical regulators* have been devised by J. W. Eichler and H. Hartig (D. R. P. 5492, 1878), and by Appold, whose instrument was a balance regulator (Proc. Roy. Soc. 1866, 15, 144).

The invention of G. J. Meurlin (D. R. P. 4703, 1878) consists of a self-regulating cone valve to control the pressure of a gas supply, and hence the temperature of a space heated by the flame. The pressure of the gas in the chamber *a* raises the cone *b* (Fig. 22), partially closing the hole in the plate *x*, and thus restricting the current. The hole in the summit of the cone *b* prevents extinction of the flame.

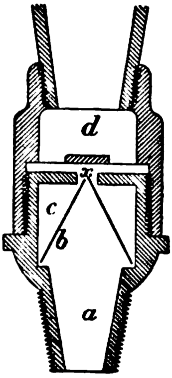


FIG. 22.

A. Schwabe (D. R. P. 93152, 1896) describes a device by which an areometer works a chain controlling the source of heat.

The choice of the type of thermostat most suitable will be governed by the requirements in each special case. Technical applications of these instruments are most frequently adequately met by the use of the simple mercury thermometer valve at moderate temperatures and the air-thermometer mercury-valve at higher temperatures, some form of differential expansion instrument being used when the liability to vibration or shock has to be provided for.

For accurate work, the reliability, sensitiveness, and independence of atmospheric changes are the most important consideration. Electrical thermostats with electrical control appear best able to fulfil the necessary conditions (*see* Geer, J. Phys. Chem. 1902, 6, 85); W. P. Bradley and A. W. Browne (*ibid.* 1902, 6, 118) claim to have constructed a thermostat sensitive to one thousandth of a degree. The toluene thermometer mercury-valve thermostat has found wide use; T. M. Lowry (J. Soc. Chem. Ind. 1905, 1030) discusses the conditions governing its sensitiveness and A. W. C. Menzies (Chem. News. 1902, 85, 68), in dealing with the same subject, shows that this type is able to keep a bath at 6° above room temperature constant within one hundredth of a degree.

The principal ways in which thermostats have been applied to technical purposes have been mentioned; recent instances of such applications are to be found in the following, not otherwise readily accessible, references.

Central heating and ventilating systems. Consolidated Car-heating Co., Wheeling, U.S.A., D. R. P. 67775, 72164, 1892; Senff, Ges. Ing. 1901, 24, 393; Johnson thermostat control of steam heating, Eng. Rec. 47, 277, 1903; Walker and Chambers, *ibid.* 47, 352, 1903; System Schultz, Ges. Ing. 27, 550, 1904; Narus-Gaye and Bloock, Met. Arb. 30, 99, 1904; Hainholzer Zugregulator, Tech. Zeit. 21, 485, 1904; Ohmes, Ges. Ing. 27, 545, 1904; Goebel, *ibid.* 28, 41, 1905; Webster, Eng. Rec. 53, 9; 54, 436, 1906; de Grahl, Ges. Ing. 29, 333, 1906; Mehl, Dingl. poly. J. 321, 698, 1906; Sc. Am. Supp. 64, 212, 1907; Pradel, El. Anz. 24, 1013, 1907; Gold Car Heating and Lighting Co., Railr. G. 2, 536, 1907; Fulton, Eng. Rec. 7, 56, 1907.

Incubators and germinating stoves. Paul. Centralblatt Bakt. 1, 29, 129, 1901; El. Rev. N. Y., 1903, 43, 941; Schlœsing, Gen. Civ. 1904, 44, 368; Joffrin, Compt. rend. 1904, 138, 817; Rogers, Centralblatt Bakt. 2, 15, 236, 1905.

Distillation or evaporation. Patterson, Chem. Ind. 21, 456, 1902; Bull. Sucr. 21, 619, 1903; Foth (fermenting worts), Z. Spiritusind. 27, 257, 1904.

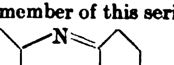
Miscellaneous. E. Clarenbach, D. R. P. 67146, 1892; Kramer, D. R. P. 67146, 1892; G. H. Stockbridge (Fire Alarm Telegraphs), Elect. London, 1896; E. Sartorius, D. R. P. 100294, 1897; R. Kanz, D. R. P. 114457, 1899; O. Bohne, D. R. P. 133429, 1899; Fedeschi, Centralblatt Bakt. 1, 30, 969, 1901; P. Breuilh, D. R. P. 150962, 1903; Regaud and Fouilliand (electric stoves), Zeit. Mikr. 20, 138, 1903; Casses (pasteurising apps.), Milch. Zeit. 33, 258, 1904; Keller and Co., Tech. Rundsch. 5, 1904; Voss, Zeit. Beleucht. 10, 216, 1904: Ginsberg, Zeit. Heiz. 9, 231, 1904; Sodeau, Chem. Ind. 23, 1134, 1904; ovens, kilns, &c., Eng. News, 51, 514, 1904; Système de Rougemont, Gén. Civ. 46, 213, 1905; damper regulator for boilers, Eng. Rec. 54, suppl. 12, 47, 1906; System Kœferle, Ges. Ing. 29, 293, 1906: Zeit. Hirz. 12, 80. 1907. W. T.

THESPASIA MACROPHYLLA (Blume) [*T. Lampas* (Dabz.).] This is a small bush common to the tropical jungles of India, Burma, and Ceylon. In Watts' Dictionary of the Economic Products of India, there is no mention of the use of this plant as a dyestuff, but, on the other hand, the capsules and flowers of the allied *T. populnea* (Soland.) are stated to give a yellow dye.

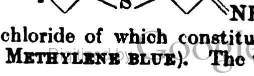
According to Perkin (Chem. Soc. Trans. 1909, 95, 1859) the flowers of the *T. macrophylla* yield quercetin and some quantity of *protocatechuic acid.*

With mordanted woollen cloth the flowers produce fairly good shades, but are in no way superior to the better-known Indian natural yellow dyestuffs. A. G. P.

THIAZINE COLOURING MATTERS. The thiazines are colouring matters containing the group

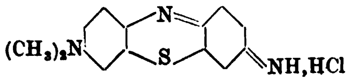


The simplest member of this series is *thionine*



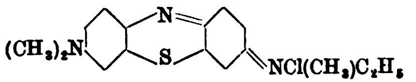
the hydrochloride of which constitutes Lauth's violet (*see* METHYLENE BLUE). The tetramethyl derivative is methylene blue (*q.v.*), which is by far the most important dyestuff of this class. The general method of preparation of these colouring matters has already been indicated (*see* METHYLENE BLUE).

Gentianine



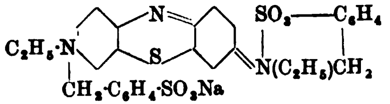
is prepared by the conjoint oxidation of *p*-phenylenediamine and dimethyl-*p*-phenylenediamine in presence of hydrogen sulphide, and comes on the market as the zinc chloride double salt. It is a reddish-brown powder which dissolves in water with a blue violet colour and dyes mordanted cotton bluish violet (Geigy and Co., Fr. Pat. 180487; U. S. Pat. 368716, 1887).

Thionine blue G



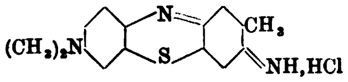
is prepared like methylene blue except that dimethyl-*p*-phenylenediaminethiosulphonic acid is oxidised together with methylethylaniline instead of dimethylaniline. It dyes tannin mordanted cotton blue.

Thiocarmine R



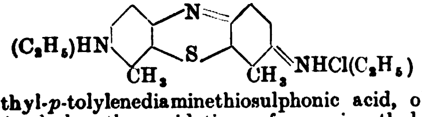
Benzylethyl-*p*-phenylenediaminesulphonic acid is oxidised in presence of sodium thiosulphate to sulphobenzylethyl-*p*-phenylenediaminethiosulphonic acid; the latter is oxidised together with benzylethylanilinesulphonic acid and the sulphoindaminethiosulphonate thus obtained is heated to boiling. The dyestuff is an indigo-blue powder giving a pure blue solution in water and dyeing wool and silk from an acid bath in blue shades (Cassella and Co., Eng. Pat. 4596, 1890; U. S. Pat. 434493; *see* also J. Soc. Chem. Ind. 1892, 11, 30).

Toluidine blue C



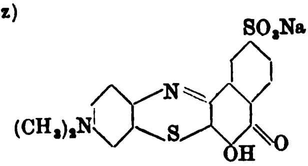
Dimethyl-*p*-phenylenediaminethiosulphonic acid (*cf.* METHYLENE BLUE) is oxidised together with *o*-toluidine. The insoluble green indamine formed is boiled with a solution of zinc chloride and the resulting leuco compound is oxidised. The colouring matter is a dark green powder giving a bluish-violet aqueous solution and dyeing mordanted cotton blue (Badische Anilin und Soda Fabrik; Eng. Pat. 10314, 1888; D. R. P. 47374; U. S. Pat. 416055; Meister, Lucius und Brüning, D. R. P. 47345).

New methylene blue N



Ethyl-*p*-tolylenediaminethiosulphonic acid, obtained by the oxidation of *p*-aminoethyl-*o*-toluidine in presence of sodium thiosulphate, is oxidised together with ethyl-*o*-toluidine and the green indamine obtained is heated. The solution of the dyestuff in water is violet-blue when cold and pure blue when hot. Tannin-mordanted cotton is dyed in redder and fuller shades than those produced by methylene blue (Cassella and Co., Eng. Pat. 8407, 1891; U. S. Pat. 469329).

Brilliant alizarin blue (Bayer); **Indochromine T** (Sandoz)



1:2-Naphthaquinone-6-sulphonic acid is condensed with dimethyl-*p*-phenylenediaminethiosulphonic acid. The dyestuff gives fast blue shades on chromed wool, cotton or silk, and is suitable for calico printing (F. Bayer and Co., D. R. P. 83046, 86717). J. C. C.

THIAZOL DYESTUFFS *v.* PRIMULINE AND ITS DERIVATIVES.

THIET-SIE. A resinous substance used as a varnish by the Burmese. It exudes from a tree in the form of a light-brown, very viscid liquid of the consistence of treacle, but on exposure to the air for a few minutes becomes quite black and hard on the surface. The same change takes place instantly in contact with potassium hydroxide. The resin spread in a thin layer on wood or other solid body quickly forms a hard deep-black coating of great brilliancy. On digesting the unaltered substance with alcohol of 80 p.c. at a gentle heat, the greater part gradually dissolves; and on decanting the clear liquid from the insoluble residue, and distilling off the alcohol, there remains a very tenacious gummy residue of a rich-brown colour, which undergoes no change of colour on exposure to the air, but very slowly hardens. In contact with potassium hydroxide, however, it blackens like the original substance.

The residue, insoluble in alcohol, dissolves for the most part in ether, forming a dark-brown solution, and leaving a light-brown solid resin. The ethereal solution, when evaporated, leaves a residue which, on exposure to the air, instantly becomes quite black, and after a short time nearly solid. This, then, is the portion of the original substance to which the property of blackening on exposure to the air is due.

The solid resin, insoluble in alcohol and ether, which forms but a small part of the original substance, is quite unalterable in the air. When heated with nitric acid, it yields a crystalline acid which may be sublimed and which exhibits the characters of succinic acid.

THIOACETAMIDE $CH_3 \cdot CS \cdot NH_2$ is prepared by the action of hydrogen sulphide on acetonitrile (Bernthsen, Annalen, 192, 46); or of phosphorus pentasulphide on acetamide in benzene solution (Hantzsch, *ibid.* 250, 264; *cf.* Hofmann, Ber. 1878, 11, 340). It crystallises in monosymmetric plates or prisms, m.p. 107·5°–108·5°, and is readily soluble in water or alcohol, less so in ether. Acids or bases decompose thioacetamide, yielding acetic acid, ammonia and hydrogen sulphide, whilst with silver nitrate solution, a precipitate of silver sulphide is obtained. It gives difficultly soluble compounds with mercuric chloride and with other metallic chlorides (Kurnakow, J. Russ. Phys. Chem. Soc. 1893, 25, 613).

THIOACETANILIDE $CH_3\cdot C(SH){:}N\cdot C_6H_5$ or $CH_3\cdot CS\cdot NH(C_6H_5)$ is prepared by the interaction of acetanilide and phosphorus pentasulphide (Jacobson, Ber. 1886, 19, 1067; Hofmann, *ibid.* 1878, 11, 339), or of the chloride of acetanilide, $CH_3\cdot CCl{:}N\cdot C_6H_5$ and hydrogen sulphide (Leo, *ibid.* 1877, 10, 2134). It crystallises from water in needles, m.p. 75°. On distillation it yields phenylamino-phenylimino-ethane

$$C_6H_5\cdot NH\cdot C(CH_3) : N\cdot C_6H_5.$$

It is soluble in sodium hydroxide solution, from which it is precipitated by the addition of acids. The sodium derivative

$$CH_3\cdot CS\cdot NNa(C_6H_5)$$

is formed by the action of sodium ethoxide. Thioacetanilide yields two series of alkyl derivatives, *viz.* the normal alkyl thioacetanilides $CH_3\cdot CS\cdot NR(C_6H_5)$ and the alkyl *iso*thioacetanilides $CH_3\cdot C(SR) : N\cdot C_6H_5$. The former are obtained by the action of phosphorus pentasulphide on alkylacetanilides, and the latter by the action of alkyl iodides on the sodium derivative of thioacetanilide.

THIOACETIC ACID CH_3COSH is best prepared by heating glacial acetic acid with phosphorus pentasulphide (Tarugi, Gazz. chim. ital. 1895, 25, i. 273; Schiff, Ber. 1895, 28, 1205; *cf.* Kekulé and Linnemann, Annalen, 123, 278; Kekulé *ibid.* 90, 311). It may also be prepared by the interaction of acetyl chloride and potassium hydrosulphide (Jacquemin and Vosselmann, J. 1859, 354), or of lead acetate and anhydrous sodium thiosulphate (Frohde, Zeitsch. Chem. 1866, 543). It is an unpleasant smelling liquid, b.p. 93°, sp.gr. 1·074 at 10°, soluble in water and in alcohol: for electrical conductivity *v.* Ostwald, Zeitsch. physikal. Chem. 3, 182. By heating in a sealed tube with water at 180°–200° or by boiling with zinc and sodium hydroxide, the sulphur is removed (Schulze, Zeitsch. physiol. Chem. 1898, 25, 16). Strong sulphuric or nitric acid reacts explosively with thioacetic acid. Phosphorus pentachloride yields acetyl chloride, phosphorus thiochloride and hydrogen chloride, whilst zinc chloride yields ethenyl trisulphide, $C_4H_4S_3$, acetic acid and hydrogen sulphide. Thioacetic acid condenses with aldehydes, ketones and ketonic acids in the presence of hydrogen chloride (Bongartz, Ber. 1886, 19, 1934). It has been recommended as a substitute for hydrogen sulphide in qualitative analysis (Schiff and Tarugi, *ibid.* 1894, 27, 3437; Tarugi and Marchionneschi, Boll. Chim. Farm. 45, 629). For *salts*, *v.* Ulrich, Annalen, 109, 275; Tarugi, Gazz. chim. ital. 1895, 25, i. 341; 1897, 27, i. 316; ii. 153.

Ethyl ester. Prepared by the interaction of acetyl chloride and ethyl hydrosulphide, but not from ethyl acetate and phosphorus pentasulphide (Michler, Annalen, 176, 182). Unpleasant smelling liquid, b.p. 116·0°–116·2° at 749·3 mm. (Beckmann, J. pr. Chem. [ii.] 17, 461).

Dithioacetic acid, *methylcarbithionic acid* $CH_3\cdot CS\cdot SH$ is prepared by the action of carbon disulphide on magnesium methyl iodide in well-cooled ethereal solution. The product is decomposed with ice and hydrochloric acid. It is a reddish-yellow oil, b.p. 37°/15 mm., sp.gr. 1·24 at 20°, readily soluble in organic solvents. It displaces acetic and formic acids from their salts. It is readily oxidised to thioacetyl disulphide by water and produces black spots on the skin. The alkali, alkaline earth, silver and magnesium salts are soluble in water, giving coloured precipitates with the salts of the heavy metals (Houben and Pohl, Ber. 1907, 40, 1303).

Methyl ester. Prepared as the acid, substituting ammonium chloride for hydrochloric acid. The product is shaken with methyl sulphate, and the red oil so formed distilled; b.p. 140°/760 mm., 80°–81°/95 mm., 71°/70 mm.; sp.gr. 1·096 at 21°/4° (Houben and Schultze, Ber. 1910, 43, 2481).

THIOANTIPYRINE or **THIOPYRINE,** $C_{10}H_{12}N_2S$. Prepared by treating the methochloride or methiodide of 1-phenyl-3-methyl-5-chloropyrazole with potassium hydrogen sulphide. Large soluble crystals, m.p. 166° (Michaelis and Bindewald, Ber. 1900, 2873).

THIOBENZENYL DYESTUFFS *v.* PRIMULINE AND ITS DERIVATIVES.

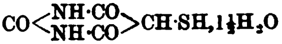
THIOBENZOPHENONE *v.* KETONES.

THIOCHROMOGEN *v.* PRIMULINE AND ITS DERIVATIVES.

THIOCOL *v.* SYNTHETIC DRUGS.

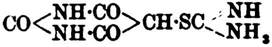
THIOCYANATES *v.* CYANIDES.

THIODIALURIC ACID

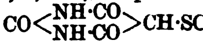


$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right\rangle\mathrm{CH\cdot SH},1\tfrac{1}{2}\mathrm{H_2O}$$

obtained by hydrolysing with dilute potassium hydroxide thio*pseudo*uric acid



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right\rangle\mathrm{CH\cdot SC}\begin{matrix}\diagup\mathrm{NH}\\ \diagdown\mathrm{NH_2}\end{matrix}$$

(Nencki, Ber. 1871, 4, 772), or potassium thiocyanobarbiturate  $\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right\rangle\mathrm{CH\cdot SCN}$ (Trzcinski, *ibid.* 1883, 16, 1057); forms bright microscopic plates. The *potassium salt* is a yellow crystalline compound, sparingly soluble in water. Thiodialuric acid dissolves in nitric acid to form a pale red solution, and on warming a violent reaction takes place and dilituric acid is formed.

THIOFLAVINE T S *v.* PRIMULINE AND ITS DERIVATIVES.

THIOFORM THIOGENOL, *v.* SYNTHETIC DRUGS.

THIOGLYCOLLIC ACID $SH\cdot CH_2\cdot CO_2H$ was first prepared by Carius (Annalen, 1862, 124, 43) by heating 3 parts of monochloracetic acid in concentrated aqueous solution with 5 parts of potassium hydrogen sulphide. Thiodiglycollic acid is formed at the same time, thus:

$$CH_2Cl\cdot CO_2H+2KSH=CH_2(SH)CO_2K+H_2S+KCl,$$
$$CH_2(SH)CO_2K+CH_2ClCO_2K=S(CH_2CO_2K)_2+HCl$$

(*v.* Claessen, *ibid.* 1877, 187, 113).

Thioglycollic acid is also formed by treating sulphochloracetylchloride, $SO_2Cl\cdot CHCl\cdot COCl$ with tin and hydrochloric acid (Siemens, Ber. 1873, 6, 659); by treating glyoxylic acid with sulphuretted hydrogen in presence of silver oxide, thiodiglycollic acid also being formed in this case (Böttinger, Annalen, 1879, 198, 215); by boiling thiohydantoïn or rhodanic acid with baryta (Andreasch, Ber. 1879, 12, 1385; Ginsburg and Bondzynski, *ibid.* 1886, 19, 117); or by treating salts of chloracetic acid with alkali or alkaline earth polysulphides and subjecting the products thus formed to the action of reducing agents (Kalle and Co., D. R. P. 180875).

Thioglycollic acid is an uncrystallisable oil, soluble in water, alcohol, and ether. It has a faint smell, acts as a strong acid and forms a number of metallic salts (Claessen, *l.c.*; Ber. 1877, 10, 1354).

If a drop of ferric chloride is added to a slightly acidified thioglycollate, a transient indigo blue colour appears, which changes to a deep violet red on adding excess of ammonia and shaking in air. On standing the colour disappears, but it is reproduced by shaking the solution with air (Andreasch, Ber. 1879, 12, 1390). Thiodiglycollic acid does not give this reaction. Thioglycollic acid reacts with aldehydes yielding compounds of the type

$$RCH(S{\cdot}CH_2{\cdot}CO_2H)_2,$$

with ketones to form the compounds

$$R_2C(S{\cdot}CH_2{\cdot}CO_2H)_2,$$

and also with ketonic acids (Bongartz, Ber. 1886, 19, 1931; *ibid.* 1888, 21, 478). It also unites with cyanamides forming hydantoïns (Andreasch, Monatsh. 1881, 2, 775; Ber. 1880, 13, 1421).

Thioglycollamide $CH_2(SH)CONH_2$ forms thin white leaflets, m.p. 149° (Holmberg, J. pr. Chem. 1905, [ii.] 71, 264).

Ethylthioglycollate $CH_2(SH)CO_2C_2H_5$, is formed by boiling the acid with absolute alcohol in the presence of a few drops of sulphuric acid (Claessen). It is an offensive smelling heavy oil, b.p. above 155° (decomp.), insoluble in water and in alcohol. For some of its derivatives, *see* Wisliscenus, Annalen, 1868, 146, 145; Heintz, *ibid.* 1865, 136, 223; Letts and Collie, J. 1878, 685.

Ethylthioglycollic acid $CH_2(C_2H_5S)CO_2H$ is formed by the interaction of ethyl chloracetate and sodium mercaptide, the ethyl ester thus formed being hydrolysed with baryta water (Claessen, Bull. Soc. chim. [ii.] 23, 444). It is an oil soluble in water, alcohol and ether, and yields metallic salts and esters. Its *amide*

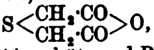
$$CH_2(C_2H_5S)CONH_2$$

has m.p. 440°.

Nitrosothioglycollic acid $(SH)CH(NO)CO_2H$ is obtained, together with cyanamide and dicyanamide, by boiling nitrosothiohydantoïn with baryta water. A number of its metallic salts have been prepared (Andreasch, Ber. 1880, 13, 601).

Dithioglycollic acid $(SCH_2{\cdot}CO_2H)_2$ forms leaflets or prisms, m.p. 100°, gives metallic salts, an *ethyl* ester, b.p. 280° (decomp.), and is reduced by zinc and hydrochloric acid to thioglycollic acid (Claessen, Ber. 1881, 14, 410; Ginsburg and Bondzynski, *l.c.*).

Thiodiglycollic acid $S(CH_2{\cdot}CO_2H)_2$ may be prepared by treating calcium chloracetate with calcium hydrogen sulphide in presence of hydrogen sulphide (Schreiber, J. pr. Chem. [ii.] 13, 472); or by mixing a concentrated aqueous solution of sodium chloracetate with an equivalent amount of sodium sulphide dissolved in the smallest quantity of water. The mixture is acidified with sulphuric acid and the thiodiglycollic acid is shaken out with ether (Lovén, Ber. 1884, 17, 2818; *ibid.* 1894, 27, 3059). It forms rhombic tablets, m.p. 129°; gives metallic salts; a *dimethyl ester,* b.p. 135°/11 mm. (Anschütz and Biernaux, Annalen, 1893, 273, 69), and a *diethyl ester*, b.p. 267°–268° (corr.) (Wislicenus, *l.c.*). Also a *chloride* $S(CH_2COCl)_2$, an *anhydride*



$S{<}\begin{matrix}CH_2{\cdot}CO\\CH_2{\cdot}CO\end{matrix}{>}O$, m.p. 102°, b.p. 158°/10 mm. (Anschütz and Biernaux, *l.c.*), and amides.

THIOINDIGO DYESTUFFS *v.* INDIGO, ARTIFICIAL, AND INDIGOID DYESTUFFS; VAT DYES.

THIOKETONES *v.* KETONES.

THIOL *v.* SYNTHETIC DRUGS.

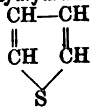
THIOLINE *v.* ABIETENE.

THIONINE *v.* METHYLENE BLUE and THIAZINE COLOURING MATTERS.

THIONURIC ACID *v.* PYRIMIDINES.

THIOPHEN. *Thiofurfuran*

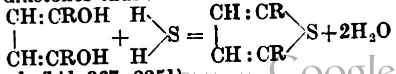
C_4H_4S or



Discovered by Victor Meyer in coal-tar benzene, which contains about 0·5 p.c. of thiophen (Ber. 1883, 16, 1465; *see* also Bull. Soc. chim. 1900, 23, 384; *ibid.* 24, 357; Heusler, Ber. 1895, 28, 488; Witzeck, Chem. Zentr. 1903, i. 1053). In order to extract the thiophen, a large quantity of the best commercial benzene was shaken for some hours with one-tenth of its volume of concentrated sulphuric acid, the black acid layer separated, diluted with water, and converted into the lead salt of the sulphonic acid thus obtained. This lead thiophen-sulphonate, which was contaminated with lead benzene-sulphonate, was dried, mixed with one-fourth of its weight of ammonium chloride, and distilled. The sulphonic acid was thus hydrolysed, and an oil passed over which was purified by shaking with caustic alkali to remove mercaptans, dried over calcium chloride and rectified.

K. E. Schulze (Ber. 1885, 18, 497) recommends that the thiophen-sulphonic acid, after diluting the crude acid with water, should be hydrolysed by steam-distillation. Thiophen may also be completely removed from commercial benzene by treating the latter with form- or acet-aldehyde or with phthalic anhydride (D. R. P. 211239; Frdl. 1908–1910, 9, 96).

According to Steinkopf (Chem. Zeit. 1911, 35, 1098), thiophen may be very readily prepared by passing acetylene over pyrites or marcasite heated to 300°, the thiophen being separated from the other products by fractional distillation. Among the products occurs a substance $C_4H_6S_2$, b.p. 36°–38° of garlic-like smell which, when treated with alkalis, loses some sulphur and also its unpleasant smell. Thiophen has been artificially prepared by numerous methods: amongst others by passing ethylene or acetylene into boiling sulphur (Victor Meyer and Sandmeyer, Ber. 1883, 16, 2176); by heating succinic anhydride with phosphorus pentasulphide, or better, sodium succinate with phosphorus trisulphide (Volhard and Erdmann, Ber. 1885, 18, 454; Friedburg, J. Soc. Chem. Ind. 1890, 1062); and in a similar way from erythrol and phosphorus pentasulphide (Paal and Tafel, Ber. 1885, 18, 688); also by the action of sulphuretted hydrogen on diketones thus:



(Paal, *ibid.* 367, 2251).

Liquid, with a faint smell. Boils at 84° (corr.), sp.gr. 1·08844 at 0°. Gives with isatin and sulphuric acid a blue colouring matter, *indophenin*, $C_{12}H_7NOS$ (test for thiophen in benzene) (Schwalbe, Ber. 1904, 37, 1244; Bauer, *ibid.* 3128). Thiophen gives similar coloured condensation products with all compounds containing the group CO·CO (*see* Denigés, Bull. Soc. chim. [iii.] 13, 538; Meyer, Ber. 1883, 16, 1473; Liebermann, *ibid.* 1887, 20, 3231; Claisen, *ibid.* 2197; Oster, *ibid.* 1904, 37, 3348). It gives an intensely red coloration with lactic acid in the presence of sulphuric acid and copper sulphate (Fletcher and Hopkins, Chem. Zentr. 1907, i. 1442), and various colours with different aldehydes (Steensma, *ibid.* 1908, i. 1492).

Thiophen may be determined by shaking 1 grm. of it with 15·15 grms. of mercuric acetate in 60 grms. of water when a white insoluble crystalline powder separates, having the composition $C_4H_4S(HgC_2H_3O_2)_4$ and which may be weighed as such. When heated with aqueous sodium chloride it yields the corresponding chloride, $C_4H_4S(HgCl)_4$, as a white insoluble microcrystalline powder. When heated with alkalis, the chloro compound yields the hydroxy derivative $C_4H_4S(HgOH)_4$ which explodes on heating, metallic mercury separating in the form of a mirror (Paolini, Gazz. chim. ital. 1907, 37, i. 58).

Thiophen may be estimated colorimetrically in benzene by charging 2 measures with 25 c.c. of isatin solution (containing 0·5 grm. isatin in 1000 grms. of pure conc. sulphuric acid) and 25 c.c. pure conc. sulphuric acid. To one of these 1 c.c. of the benzene to be tested is added, to the other 1 c.c. of a test solution containing a definite quantity (from 0·01–0·5 p.c.) of thiophen in benzene and the colours after shaking for 5 minutes are compared on a white base (Schwalbe, Chem. Zeit. 1905, 29, 895).

When boiled with aluminium chloride, thiophen forms an insoluble resin (Heusler, Zeitsch. angew. Chem. 1896, 11, 750; Bödtker, Compt. rend. 1896, 123, 310; Haller and Michel, Bull. Soc. chim. 1896, 15, 1065).

Thiophen combines with mercuric chloride and sulphate (Dimroth, Chem. Zentr. 1901, i. 450; Schwalbe, Ber. 1905, 38, 2208), and also with the acetate as above.

A small quantity of thiophen, mixed with vanillin and concentrated sulphuric acid gives a green or bluish-green colour. A green colour is also formed gradually when wood is moistened with 1–2 drops of thiophen and 10 times the amount of alcohol mixed with an equal volume of sulphuric acid is added (Ihl, Chem. Zeit. 14, 1707). According to Thomas (Bull. Soc. chim. 1909, [iv.] 5, 182, 736), pure thiophen is not reduced by Sabatier and Senderens' method.

When treated with hydrogen peroxide (1–3 p.c. solution), thiophen yields *oxythiophen* $C_4H_4O_2S$, b.p. 130°, and *tetraoxythiophen*, b.p. 158°–160°. Both have a pleasant smell, a burning taste, and give a green coloration with isatin and sulphuric acid. If 25 p.c. hydrogen peroxide is used the oxythiophens are decomposed forming sulphuric acid and yellow resinous products (Lanfry, Compt. rend. 1911, 153, 73).

Both in its physical properties and in its chemical reactions, thiophen closely resembles benzene. Benzene boils at 80°, thiophen at 84°. Like benzene it combines with certain substances as thiophen of crystallisation (Liebermann, Ber. 1893, 26, 853; Prokofjeff, J. Russ. Phys. Chem. Soc. 1897, 29, 87). The halogens, nitric acid, and sulphuric acid react with thiophen, yielding substitution products corresponding with and very similar in properties to those of benzene, excepting that thiophen, owing to its unsymmetrical constitution, forms *two* series of mono-substitution compounds—α-compounds, in which a hydrogen atom adjacent to sulphur is replaced, and β-compounds, in which the substitution takes place with a hydrogen atom in the meta- position to sulphur (Bamberger, Ber. 1897, 30, 369; Willgerodt, J. pr. Chem. 1886, 33, 150; Rosenberg, Ber. 1886, 19, 650; Schleicher, *ibid.* 1885, 18, 3015; Ciamician and Angelli, *ibid.* 1891, 24, 74, 1347, Marcusson, *ibid.* 1893, 26, 2457; Töhl and Schultz, *ibid.* 1894, 27, 2834; *ibid.* 1895, 28, 2217; Eberhard, *ibid.* 2385).

Thiophen diiodide $C_4H_2I_2S$ forms crystalline plates, m.p. 40·5°, and is sometimes used as a substitute for iodoform in surgical cases.

In the presence of anhydrous ether, magnesium dissolves in 2-iodothiophen giving magnesium thiophen iodide which reacts with ketones forming tertiary alcohols, some of which products are described by Thomas (Compt. rend. 1908, 146, 642; *see* also Tschelinzeff, Chem. Zentr. 1905, i. 146).

Sodium thiophen sulphonate $C_4H_3S{\cdot}NaSO_3$ is a white crystalline powder which has been employed in prurigo, being non-toxic and non-irritant: it has proved more effective than β-naphthol. Nitrothiophen (Stadler, Ber. 1885, 18, 530), like nitrobenzene, yields, with reducing agents, the corresponding amino compound (Stadler, *ibid.* 1490; 2316; Goldschmidt and Schulthess, *ibid.* 1887, 20, 1701).

Homologues of thiophen are present in coal-tar benzene and may be separated by methods similar to those used for separating thiophen (Messinger, Ber. 1885, 18, 563, 1636; Keiser, *ibid.* 1896, 29, 2560). Many of these α- and β-homologues are known and may be obtained by a variety of synthetic methods. By treating a mixture of 2-iodo-thiophen and methyl iodide with sodium, 2-*methylthiophen* (thiotolene) can be obtained (Kues and Paal, Ber. 1886, 19, 555; Meyer and Kreis, *ibid.* 1884, 17, 1558). 2-*Ethyl thiophen* may be obtained similarly. For various homologues and their halogen and other derivatives, *see* Grünwald (Ber. 1887, 20, 2585); Zelinsky (*ibid.* 2017; *ibid.* 1888, 21, 1835); Thiele (Annalen, 1892, 267, 133); Opolski (Chem. Zentr. 1905, i. 1255; *ibid.* ii. 1796) amongst others.

2-*Phenylthiophen* is obtained by distilling β-benzoylpropionic acid or benzoylisosuccinic acid with phosphorus tri- or penta-sulphide (Kues and Paal, *ibid.* 1886, 19, 3142). It crystallises in small plates, m.p. 40°–44°.

3-*Phenylthiophen* is obtained by the interaction of thiophen and nitrosoacetanilide. The compound obtained by Möhlau and Berger (*ibid.* 1893, 26, 2001) from diazobenzene chloride and thiophen in the presence of aluminium chloride is a mixture of 2- and 3-phenylthiophens (Bamberger, *ibid.* 1897, 30, 36). 3-Phenylthiophen crystallises in plates, m.p. 90°–90·5°, b.p. 254°–260°. Renard (Compt. rend. 1889, 109,

699) describes another phenylthiophen, m.p. 330°, which was obtained by passing a mixture of the vapours of toluene and sulphur through an iron tube heated to redness.

Diphenyl-, *ditolyl-*, and other diarylthiophens may be obtained by heating mixed aliphatic aromatic ketones in the presence of water and ammonium sulphide at 215° under pressure (Willgerodt and Scholtz, Chem. Zentr. 1910, i. 1969). For another method of obtaining the diphenylthiophens, *v.* Baumann and Fromm (Ber: 1895, 26, 2001).

Dinaphthathiophen $C_{20}H_{12}S$, and *benzdithiophen* $C_{10}H_6S_2$, have been isolated from the product obtained from the interaction of the vapours of sulphur and naphthalene at a red heat. The former crystallises in pearly yellow scales, melts at 250·5° (corr.), and boils above 440°. It yields a hexabromo derivative $C_{20}H_6Br_6S$, m.p. 260°, and a tetranitro derivative

$$C_{20}H_8(NO_2)_4S,$$

m.p. 210° (*circa*). Oxidation with chromic acid gives phthalic acid. The latter crystallises in ruby red leaflets, melts at 118·5° (corr.), and boils at 345°. It gives the thiophen reaction with sulphuric acid and isatin. From it a tetrabromo derivative $C_{10}H_2Br_4S_2$, m.p. 247°–248°, and a tetranitro derivative $C_{10}H_2(NO_2)_4S_2$, decomposing at 300°, have been obtained (Lanfry, Compt. rend. 1911, 152, 92, 1254). Other naphthalenethiophens have been described by Dziewonski (Bull. Soc. chim. 1904, [iii.] 31, 925).

Dithiënyl $(C_4H_3S)_2$, m.p. 83°, is formed when the vapour of thiophen is passed through a red-hot tube, just as diphenyl $(C_6H_5)_2$ is formed under these conditions from benzene (Nahnsen, Ber. 1884, 17, 789). Töhl (*ibid.* 1894, 27, 665) obtained another dithiënyl, m.p. 33°, by the action of anhydrous feebly fuming sulphuric acid on ice cold thiophen. A third dithiënyl, m.p. 132°, was obtained by Auwers and Predt (*ibid.* 1741) by heating butane tetracarboxylic acid with phosphorus sulphide.

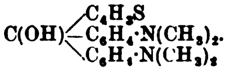
Thiophen carboxylic acids may be obtained by oxidising the corresponding alkyl thiophens and also by various other methods (Nahnsen, Ber. 1884, 17, 2197; Peter, Ber. 1885, 18, 542; Messinger, *ibid.* 563; Nahnsen, *ibid.* 2304; Schleichter, *ibid.* 3015; Damsky, *ibid.* 1886, 19, 3282; Levi, *ibid.* 656; Curtius, Chem. Zentr. 1902, i. 457; Holleman and Voerman, Proc. K. Akad. Wentesch. Amsterdam, 1907, 9, 514; Rec. trav. chim. 1907, 26, 293; Schorigin, Ber. 1910, 43, 1938). Thiophen-2-carboxylic acid, m.p. 126°–127°; thiophen-3-carboxylic acid, m.p. 136°; and three dicarboxylic acids are known.

Thiophen aldehyde $C_4H_3S{\cdot}CHO$, a pale yellow oil, b.p. 198°, having a pleasant smell, is obtained by the distillation of α-thienylglyoxylic acid $C_4H_3S{\cdot}CO{\cdot}CO_2H$ (Biedermann, Ber. 1886, 19, 1853) or by the action of sulphuretted hydrogen on chlordiketopentamethylene

$$\begin{matrix}CH_2\text{—}CHCl\\CH_2\text{——}CO\end{matrix}\!\!>\!CO$$

(Hantzsch, *ibid.* 1889, 22, 2838: Hantzsch and Witz, *ibid.* 1901, 34, 841). On oxidation it yields the α-acid. Many of its derivatives are known. Thiophen ketones and a large number of other derivatives of thiophen have been prepared.

Thiophen green



$$C(OH)\begin{cases}C_4H_3S\\C_6H_4{\cdot}N(CH_3)_2\\C_6H_4{\cdot}N(CH_3)_2\end{cases}$$

This compound, which was discovered by L. E. Levi (Ber. 1887, 20, 513), is an analogue of malachite green. The leuco base

$$CH(C_4H_3S)[C_6H_4{\cdot}N(CH_3)_2]_2$$

is first prepared by heating a mixture of one part of thiophenaldehyde, 2 parts of dimethylaniline with a little alcohol, and 3 to 4 parts of zinc chloride for 6 hours, adding the zinc chloride gradually, and, if the mass becomes thick, diluting slightly with water. The product is made alkaline with caustic soda, steam-distilled, extracted with ether, and the crystalline residue which is left on evaporating the ether recrystallised from alcohol. This crystalline leuco base is then oxidised with manganese dioxide and dilute sulphuric acid, when it yields thiophen green. The colouring matter is extracted with hot water, filtered from manganese dioxide, precipitated with ammonium chloride and ammonia, and extracted with ether. It is, as represented by the formula, the carbinol corresponding with the leuco base. Like malachite green, it forms a double salt with zinc chloride. It dyes silk and wool a shade very much like that of malachite green, but somewhat yellower.

W. Krause (Internat. Monatschr. Anat. u. Physiol. 4, 2; J. Soc. Chem. Ind. 1887, 507) recommends the use of the zinc double salt of thiophen green for staining sections, especially as a complementary colour to carmine. It dissolves readily in water, alcohol, and chloroform, but is insoluble in benzene.

THIOSEMICARBAZIDE *v.* HYDRAZINES.

THIOSTANNIC ACID *v.* TIN SALTS AND OXIDES.

THOMAS SLAG *v.* FERTILISERS.

THORIANITE. A heavy, black mineral consisting of thoria (51–80 p.c.) with uranium oxides (11–32·7 p.c.), &c. It is isomorphous with pitchblende (*q.v.*) and very similar to the crystallised varieties of this in most of its characters. The principal difference between the two minerals is in the relative amounts of the thorium and uranium oxides, thorianite being essentially $(Th,U)O_2$ and pitchblende $(U,Th)O_2$. Thorianite is known only from Ceylon, where it is found in the stream-beds and in the gem-bearing alluvial gravels at several spots in the Central, Sabaragamuwa, and Southern provinces. The heavy minerals occurring with it, and separated by the gemmers from the alluvia by a simple process of washing, are zircon, ilmenite, thorite, gold, &c. The largest amounts have been obtained from the Kuda Pandi-oya, a small stream in the Bambarabotuwa district, about 20 miles from Balangoda in the Sabaragamuwa province; but the deposits are of limited extent, and soon become exhausted. The occurrence of the mineral *in situ* has also been noted at one or two places (Gampola and Maddegama) in Central province, a few crystals having been found in pegmatite-veins. Prospecting for the original sources is, however, difficult, owing to the thick growths of jungle.

Thorianite is found as small, simple cubes, usually only a few mm. across, and only exceptionally reaching 2 or 3 cm. Interpenetratio twins, like those of fluor-spar, are occasionally met with. The colour is jet-black, and, when the surface is not water-worn and dulled, the lustre is bright and pitchy. The streak is brown with a tinge of green; thin sections are translucent and optically isotropic. The high sp.gr. of about 9·5 is a striking feature; hardness nearly 7. The mineral is soluble in nitric acid and in sulphuric acid, but is scarcely attacked by hydrochloric acid. It is the richest known source of helium, 8·2–9·5 c.c. per gram being given off when the mineral is heated or dissolved in acid. Its radioactivity is less than that of pitchblende, there being less radium but more radiothorium. Nipponium and some other possibly new elements have been extracted from thorianite (M. Ogawa, 1908: C. de B. Evans, 1908).

Analysis I. of thorianite from near Balangoda (W. R. Dunstan and B. M. Jones, Proc. Roy. Soc. 1906, A, 77, 546). II. same locality (Dunstan and G. S. Blak·, *ibid.* 1905, A, 76, 253). III. ditto (Dunstan, Nature, 1904, 69, 510). IV. ditto (E. H. Büchner, Proc. Roy. Soc. 1906, A, 78, 385). V. and VI. from Galle, Southern province (Dunstan and Jones, *l.c.*).

	I	II[1]	III[2]	IV[3]	V	VI
ThO_2	78·98	78·86	72·24	70·96	62·16	58·84
UO_2	13·40	6·03	11·19	13·12	10·32	32·74
UO_3		9·07			18·88	
Ce_2O_3	1·47	1·02	6·39	1·96	1·84	0·85
$(La,Di)_2O_3$		—	0·51			
PbO	2·54	2·59	2·25	2·42	2·29	2·56
Fe_2O_3	0·87	0·46	1·92	2·05	1·11	1·31
CaO	0·91	1·13	—	0·13	0·59	0·19
H_2O	1·28	—	—	3·20	1·05	1·26
Insol.	0·47	0·20	0·41	—	0·77	0·45

Thorianite contains a higher percentage of thoria than any other known mineral, and it has been employed as a source of thoria for use in incandescent gas mantles. The amount exported from Ceylon in 1905 was about 9 tons, which sold for £1600 to £1700 per ton; since then, however, the price of thoria has fallen considerably.

For local details of occurrence, &c., *see* Administration Reports, Ceylon, Colombo, 1904, &c.; Colonial Reports, Miscell. Ser., Ceylon Mineral Survey, London, 1904, &c.

L. J. S.

THORITE. A mineral consisting essentially of thorium silicate, $ThSiO_4$, crystallising in the tetragonal system and isomorphous with zircon. Analyses show: SiO_2, 12–19; ThO_2, 48–74 (the formula requires 81·5); U_2O_3, 1–10; Ce_2O_3, 0–3; H_2O, 6–10 p.c. The presence of water appears to be due to secondary alteration; and the fact that the mineral is frequently optically isotropic and amorphous indicates that it is not fresh. The colour is yellow to dark brown, and in the orangite variety (*q.v.*) a bright orange-yellow; the lustre is resinous; sp.gr. 4·4–5·4. The mineral occurs as small masses and indistinct crystals in the augite-syenite on the Langesund-fjord and near Arendal, and a few other places in the south of Norway. It is also found, together with thorianite, in the gem-gravels of Ceylon. Small amounts are collected for the preparation of thorium compounds and used principally for the mantles of incandescent gas-lights. L. J. S.

THORIUM. Sym. Th. At.wt. 232·4. This element, which has the highest atomic weight of the metals of the rare earth series, was identified by Berzelius in 1829 as occurring in the form of silicate in the mineral thorite, obtained from the island of Löv-ön (near Brevig, Norway).

Occurrence.—Thoria is present as the main constituent in thorite, orangite, and their alteration products, mackintoshite, auerlite, calciothorite, and freyalite, and in thorianite (Dunstan and Jones, Proc. Roy. Soc. 1905, 76 A, 253: 1906, 77 A, 546; Szilard, Compt. rend. 1907, 145, 463). It occurs in variable amounts (1–18 p.c.) in monazite, and yttrocrasite (Amer. J. Sci. 1906, [iv.] 22, 515).

Extraction and Purification.

1. *Separation from thorite, orangite,* and *thorianite.* These minerals are easily decomposed by the strong mineral acids when silicic acid separates, and the solution containing the metallic constituents is freed from lead, bismuth, &c., by hydrogen sulphide. Thorium is then separated in the form of its octahydrated sulphate $Th(SO_4)_2,8H_2O$, which separates from aqueous solutions below 47°. This salt is redissolved in water, and oxalic acid added to precipitate thorium oxalate, which is then ignited to thoria and the cycle of operations repeated (Krüss and Nilson, Ber. 1887, 20, 1665).

Thorium salts may be separated from those of the cerite metals by dissolving in alkali carbonates or oxalates. But this process brings into solution also small amounts of the ytterbite metals, which, however, do not occur in thorium minerals to any large extent. Solutions of thorium salts readily undergo hydrolytic change when boiled with sodium thiosulphate, thorium hydroxide being precipitated mixed with sulphur; this operation separates thorium from all rare earth metals excepting scandium and zirconium (Bunsen, Pogg. Ann. 1875, 155, 379; Moissan and Étard, Compt. rend. 1896, 122, 573; Urbain, Bull. Soc. chim. 1896, [iii.] 15, 338; Brauner, Chem. Soc. Trans. 1898, 73, 951).

2. *Separation from monazite sand.* Monazite, an orthophosphate of the cerite metals which contains varying proportions of thorium, is very widely diffused in the earth's crust, occurring primarily as an accessory constituent of certain plutonic rocks (granites, diorites, gneisses, &c.). It is, however, chiefly in its secondary form of monazite sand that the mineral is exploited for the gas-mantle industry. The erosive action of rivers and tides on the original monazite containing rocks gives rise to enormous accumulations of monazite sands found in littoral and fluviatile deposits chiefly in Brazil (Bahia and Minas Geraes) and in North and South Carolina. Less extensive strata are found in Australia and the Ural Mountains, and certain deposits on the coast of Travancore have acquired some importance.

In addition to the yellow grains of monazite, the sand contains fragments of magnetite, chromite, titanite, quartz, felspar, hornblende, rutile, brookite, zircon, and small quantities of rare-earth minerals (*e.g.* samarskite, æschynite).

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[1] Also He, 0·39.

[2] Also ZrO_2, 3·68 (due to enclosed zircon); SiO_2, 1·34; sp.gr. 8·98.

[3] Also ZrO_2, 0·23; SnO_2, 0·05; Sb_2O_4, 0·11; Al_2O_3, 15; etc.

After some preliminary mechanical or magnetic dressing the monazite sand is decomposed by heating with concentrated sulphuric acid, and the product dissolved in cold water, the residue containing the unattacked constituents of the sand, quartz, zircon, titanite, &c. The acid solution is partially neutralised with magnesia, sodium hydroxide or ammonia until precipitation of the phosphates of the rare-earth metals occurs, when thorium phosphate, being the least soluble of this series, is concentrated in the first fractions. The phosphate is dissolved in strong hydrochloric acid and the thorium reprecipitated by oxalic acid.

The sparing solubility of thorium oxalate in solutions containing excess of mineral acid serves also to separate thorium from the commoner metals (iron, manganese, calcium, &c.).

The thorium oxalate in the precipitate when warmed with aqueous sodium carbonate passes into solution together with small quantities of any ytterbite metals present. The cerite metals remain for the chief part undissolved in the form of double carbonates.

The thorium in the carbonate solution is reprecipitated either as oxalate by adding acid or as hydroxide by adding caustic soda. Further purification is effected by converting the oxalate or hydroxide into sulphate and crystallising repeatedly the octahydrated salt (Koppel and Holtkamp, Zeitsch. anorg. Chem. 1910, 67, 266).

A method similar in principle to the foregoing is based on the employment of normal sodium sulphite when salts of thorium (and zirconium) form double sulphites

(*e.g.* $Th_2(OH)_2(SO_3)_3,2Na_2SO_3,22H_2O$)

soluble in excess of aqueous alkali sulphite, whereas the cerite metals remain for the most part undissolved (Chavastelon, Compt. rend. 1900, 130, 781; Grossmann, Zeitsch. anorg. Chem. 1905, 44, 229; Batěk, *ibid.* 45, 87).

Hydrated thorium peroxide is precipitated by hydrogen peroxide from acid solutions of thorium salts, but in presence of cerite metals a certain amount of cerium is co-precipitated. The operation must be repeated several times to effect a complete separation (Wyrouboff and Verneuil, Bull. Soc. chim. 1898, [iii.] 19, 219; Compt. rend. 1898, 127, 412).

A separation of thorium and zirconium from the cerium and yttrium elements is brought about by stirring thoroughly into a dilute solution of the nitrates (containing tervalent cerium) an excess of freshly-prepared lead carbonate. After 12 hours the hydrates of thoria, zirconia, and ferric oxide are completely precipitated, the hydroxides of aluminium, chromium, and uranium are partially deposited, whilst cerium, yttrium, and other rare earth metals remain in solution. The precipitate is redissolved and the thoria present is further purified (Giles, Chem. News, 1905, 92, 130). The sparingly soluble basic acetate (Böhm, Die Darstellung der seltenen Erden, vol. i. 40, 1290), and the chromate (Ber. 1900, 33, 2028) have been recommended for separating thorium from the cerite metals. The acetylacetonate may be employed in purifying small quantities of thoria; the well-dried salt is extracted with chloroform, in which thorium acetylacetonate alone dissolves (Urbain, Bull. Soc. chim. 1896, [iii.] 15, 338, 347; Ann. Chim. Phys. 1900, [vii.] 19, 184). Repeated precipitation of thorium by potassium azide is recommended as a mode of separation and purification (Dennis and Kortright, Amer. Chem. J. 1894, 16, 79; J. Amer. Chem. Soc. 1896, 18, 947).

m-Nitrobenzoic acid precipitates thorium quantitatively as thorium *m*-nitrobenzoate in presence of aniline or from neutral solutions of the rare-earth nitrates derived from monazite, and a repetition of the process affords a complete separation from cerium, lanthanum, neodymium, and praseodymium, but the first of these elements must be in the tervalent condition, otherwise the sparingly soluble yellow ceric *m*-nitrobenzoate is deposited (J. Amer. Chem. Soc. 1904, 26, 780; Zeitsch. angew. Chem. 1905, 18, 92). This method avoids the use of alcohol, which is required in the separation of these metals with fumaric acid.

Certain organic bases have a selective action in the precipitation of the hydroxides of the rare earths; *p*-toluidine separates thorium and zirconium from lanthanum, neodymium, and praseodymium, whilst hexamethylenetetramine and the chloranilines serve to separate thorium from zirconium (Hartwell, J. Amer. Chem. Soc. 1903, 25, 1128).

The resolution of thoria into three chlorides differing in volatility and containing respectively three elements with different atomic weights has not been confirmed (Baskerville, *ibid.* 1904, 26, 922; Ber. 1905, 38, 1444; *cf.* R. J. Meyer and Gumperz, *ibid.* 1905, 38, 817; Eberhard, *ibid.* 38, 826).

Metallic thorium. The isolation of the metal in a pure state is a matter of considerable difficulty owing to its infusibility, and to its power of combining with nitrogen, hydrogen, carbon, silicon, and the metals. The reduction of thoria with magnesium is not complete (Ber. 1891, 24, 873); the action of silicon and aluminium on thoria or on potassium thorium fluoride leads respectively to the formation of a silicide $ThSi_2$, and an alloy $ThAl_3$ (Compt. rend. 1906, 142, 157, 280). Reduction of the chloride or double potassium chloride with sodium at red heat in an iron cylinder gives a product still containing thoria. A rolled specimen of metal obtained in this way melted at 1450° and had sp.gr. 12·14 (Ber. 1883, 16, 153; Compt. rend. 1883, 96, 346; Ann. Chim. Phys. 1906, [viii.] 8, 182; Zeitsch. Elektrochem. 1908, 14, 768). Electrolysis of thorium chloride dissolved in a fused mixture of sodium and potassium chlorides contained in a graphite crucible afforded a product melting at 1700° (*ibid.* 1909, 15, 866). Alloys of thorium are obtained by reducing, with sodium or with carbon and sodium hydroxide, mixtures of thorium salts with those of more fusible metals (Sn, Pb, Sb, Al, or Cu), and thorium fluoride heated with tin or lead gives thorium alloys of these metals (D. R. P. 146503).

Reduction of thoria by amorphous boron leads to the formation of two *thorium borides*, ThB_4, prismatic crystals, sp.gr. 7·5 at 15°, and ThB_6, reddish-violet mass, sp.gr. 6·4 at 15°: the former is soluble and the latter insoluble in concentrated hydrochloric acid (Compt. rend. 1905, 141, 191).

Colloidal thorium is prepared by rubbing 95–96 p.c. thorium with cold dilute hydrochloric acid and washing the mass on a filter until a grey opalescent solution passes through; this liquid is stable to acids, but not to alkalis. On electrification the thorium particles are found to carry a positive charge (Zeitsch. Chem. Ind. Kolloide, 1909, 5, 191).

Thorium hydride ThH_4, produced by direct combination of the metal and hydrogen at red heat, or by absorption of the gas by a heated mixture of thoria and magnesium. It is not decomposed by water, but evolves hydrogen on treatment with hydrochloric acid (Ber. 1891, 24, 873; Compt. rend. 1900, 131, 891; 1901, 132, 36; Ann. Chim. Phys. 1907, [viii.] 10, 130).

Thorium carbide ThC_2, yellow microscopic crystals, sp.gr. 8·96 at 18°, prepared by heating an intimate mixture of thoria and carbon in the electric furnace (900 ampères, 50 volts), is decomposed by cold water evolving acetylene, methane, ethylene, and hydrogen (Compt. rend. 1893, 116, 1227; 1896, 122, 573; Ann. Chim. Phys. 1897, [vii.] 12, 427).

Thorium silicide $ThSi_2$, quadratic plates, sp.gr. 7·96/16°, produced by heating to 1200° a mixture of potassium silico- and thoro-fluorides and aluminium (Chem. Zeit. 1906, 29, 1031; Compt. rend. 1906, 142, 157).

Thorium nitride Th_3N_4, brown powder, obtained by direct union of its components at high temperatures; by heating a mixture of thorium and ammonium chlorides in hydrogen chloride, or by passing ammonia over heated thorium carbide; it is decomposed by water with evolution of ammonia (Compt. rend. 1896, 122, 573; 1900, 131, 837; 1901, 132, 36: Ann. Chim. Phys. 1897, [vii.] 12, 427; 1907, [viii.] 10, 130).

Thorium sulphide ThS_2, dark-brown lamellæ sp.gr. 6·7 at 0°, and **thorium oxysulphide** ThOS, yellow crystalline powder, sp.gr. 8·42 at 0°, are produced by passing hydrogen sulphide over a mixture of thorium chloride and excess of sodium or potassium chloride at red heat (Compt. rend. 1908, 146, 815; *cf.* Zeitsch. anorg. Chem. 1907, 53, 74).

Thorium fluoride ThF_4, white amorphous powder, resulting from the interaction of hydrogen fluoride and thorium chloride or bromide at 354°–400° (Compt. rend. 1908, 146, 973). The *hydrate* $ThF_4,4H_2O$, a gelatinous precipitate, obtained on adding hydrofluoric acid to solutions of thorium salts, changes to a heavy white powder, the insolubility of which in excess of the precipitant serves as a separation of thorium from zirconium (Bull. Soc. chim. 1897, [iii.] 20, 69); *double fluorides* have been prepared approximating to the composition $KTh_2F_9,6H_2O$ and $KThF_5,H_2O$, and not to the typical fourth-group formula $K_2R^{IV}F_6$ (Zeitsch. anorg. Chem. 1903, 35, 424).

Thorium chloride $ThCl_4$ can be prepared by the following methods, but unless oxygen and moisture are carefully excluded, the product is always contaminated with oxychloride: (i.) heating metallic thorium in hydrogen chloride (Ber. 1887, 20, 1665; Zeitsch. physikal. Chem. 1887, 1, 301); (ii.) heating thoria in carbon tetrachloride vapour or in a mixture of carbon monoxide and chloride (Compt. rend. 1901, 132, 36, 1908; 147, 1046; Ann. Chim. Phys. 1907, [viii.] 10, 130); (iii.) heating thoria in chlorine saturated with sulphur chloride (Compt. rend. 1904, 138, 631; *cf.* Ber. 1905, 38, 817); (iv.) decomposing the heated carbide with chlorine (Compt. rend. 1905, 140, 1510). When purified by sublimation *in vacuô* (720°–750°) the chloride is obtained in colourless needles or prisms, sp.gr. 4·59, m.p. 820°.

Thorium oxychloride $ThOCl_2$ is an intermediate product obtained in the foregoing operation (No. ii.); it crystallises from alcohol and absorbs $6H_2O$ from moist air. The *hydrate* $ThCl_4,8H_2O$ is readily soluble in water or alcohol, and the soluble *hydroxy-chlorides* $Th(OH)Cl_3,7H_2O$ and $Th(OH)_2Cl_2,5H_2O$ have been isolated.

Thorium chloride combines with ammonia to form several additive compounds, of which $ThCl_4,4NH_3$ alone is stable above 120° (Compt. rend. 1910, 151, 387). Additive compounds are also formed with organic bases and with alcohols and aldehydes (Zeitsch. anorg. Chem. 1903, 35, 424; Ber. 1904, 37, 3662).

Thorium bromide $ThBr_4$, transparent colourless needles, sp.gr. 5·62, unstable in the light, evolving bromine, boils at 725° and sublimes *in vacuô* at 600°–620° (Compt. rend. 1905, 140, 1510; 1907, 145, 243).

Thorium platinocyanide $Th[Pt(CN)_4]_2,16H_2O$, yellow rhombic prisms from thorium sulphate and barium platinocyanide.

Thorium hydroxide $Th(OH)_4$, heavy white powder, readily soluble in mineral acids or in aqueous alkali carbonates. The hydrosol form of this hydroxide is produced by dialysing solutions of thorium nitrate or by adding thorium nitrate solution gradually to the well-washed hydrosol and boiling the mixture until an opalescent solution is obtained. Thorium hydroxide hydrogel is also converted into the hydrosol form by diluted (N/20) hydrochloric acid, or by solutions of aluminium or ferric chloride (Biltz, Ber. 1902, 35, 4436; 1904, 37, 1100; Müller, *ibid.* 39, 2857; Zeitsch. anorg. Chem. 1908, 57, 314; J. Chim. Phys. 1907, 5, 488, 495).

The so-called *thorium meta-oxide* is a soluble modification of thoria, produced by igniting the oxalate or hydroxide at comparatively low temperatures and evaporating the residue with hydrochloric or nitric acid until a syrup is left, which dissolves in water to a milky solution, appearing yellow by transmitted light (Cleve, Jahrb. Min. 1874, 161; Stevens, Zeitsch. anorg. Chem. 1901, 27, 41; Wyrouboff and Verneuil, *ibid.* 28, 90; Compt. rend. 1898, 127, 863).

Thorium dioxide (*thoria*) ThO_2, white powder, sp.gr. 10·220 at 17°, is obtained by igniting the hydroxide or the thorium salts of volatile acids.

Thorium peroxide is a gelatinous white precipitate, retaining acid and of somewhat uncertain composition, formed by adding hydrogen peroxide to solutions of thorium salts; its peroxide character is manifested by the liberation of iodine from potassium iodide (Compt. rend. 1898, 126, 340; Bull. Soc. chim. 1898, [iii.] 19, 219; Ann. Chim. Phys. 1906, [viii.] 6, 441; Zeitsch. anorg. Chem. 1900, 25, 378; 1902, 31, 359; R. Accad. Sci. Torino. 1911, 46, 195).

Thorium sulphate $Th(SO_4)_2$, obtained in the anhydrous condition by treating thoria with concentrated sulphuric acid, dissolves in ice-cold water to a 25 p.c. solution, which is supersaturated at all temperatures from 0° to 100° and yields between 0° and 43° (or 47° ?) either spontaneously or after seeding, monoclinic prisms of the *nonahydrate* $Th(SO_4)_2,9H_2O$, and above the latter temperature needles of the *tetrahydrate* $Th(SO_4)_2,4H_2O$; these hydrates are isomorphous with the corresponding uranous compounds $U(SO_4)_2,9H_2O$ and $U(SO_4)_2,4H_2O$ (Zeitsch. Krist. 1900, 32, 250; 1901, 34, 307).

The *octahydrate* $Th(SO_4)_2,8H_2O$, prismatic crystals, separates under conditions similar to those which favour the formation of the more stable nonahydrate, and owes its production to the existence of a metastable phase having a very low velocity of transformation (Bull. Soc. chim. 1901, [iii.] 25, 105; Bull. Soc. Min. 1901. 24, 105; Ber. 1887, 20, 1665; 1905, 38, 817).

The *acid sulphate* $ThSO_4(HSO_4)_2$, needles, is obtained by drying *in vacuô* at 130°, the product of the action of concentrated sulphuric acid on a saturated solution of the anhydrous normal sulphate (Zeitsch. anorg. Chem. 1904, 38, 322); a *hydrated acid sulphate* $2Th(SO_4)_2,H_2SO_4,2H_2O$ (Gazz. chim. ital. 1903, 32, ii. 523); and a *basic sulphate* $ThOSO_4,2H_2O$ (Compt. rend. 1883, 96, 1860; 1910, 151, 70; Ber. 1910, 43, 2776) have been described. The following *double sulphates* have been isolated: $K_4Th(SO_4)_4,2H_2O$, sparingly soluble; $K_8Th(SO_4)_6,2H_2O$; the corresponding ammonium salt series;

$Rb_2Th(SO_4)_3,2H_2O$;

$Cs_2Th(SO_4)_3,2H_2O$; $Na_2Th(SO_4)_34$ and $12H_2O$ (Bull. Soc. Min. 1901, 24, 105; Zeitsch. anorg. Chem. 1903, 35, 424; Gazz. chim. ital. 1903, 32, ii. 523).

Thorium nitrate $Th(NO_3)_4$, with 5, 6, and $12H_2O$, the dodecahydrate separating in hygroscopic plates (Cleve, *l.c.*; *cf.* Zeitsch. angew. Chem. 1897, 115; Chem. Soc. Trans. 1898, 73, 951). The commercial product, which is not a definite hydrate, but approximates to $Th(NO_3)_4$ with $4H_2O$, swells up considerably on ignition, leaving a finely divided residue of snow-white thoria. Commercial thorium nitrate should contain from 48 to 50 p.c. of ThO_2; a considerably higher percentage of oxide indicates the presence of yttrium metals.

Thorium nitrate unites with the nitrates of univalent and divalent metals, forming complex nitrates, having respectively the general formulæ $R_2'Th(NO_3)_6$ and $R''Th(NO_3)_6,8H_2O$, which correspond with the double nitrates containing quadrivalent cerium. Similar double nitrates (and sulphates) are formed with organic bases (Zeitsch. anorg. Chem. 1901, 27, 359; 1908, 60, 123).

Complex thorium carbonates. Normal thorium carbonate is not known, but complex carbonates are prepared by adding soluble carbonates to thorium solutions until the precipitate first formed redissolves or by dissolving thorium hydroxide in aqueous alkali bicarbonate, saturated with carbon dioxide; the product is precipitated by alcohol. *Sodium thorium carbonate* $Na_6Th(CO_3)_5,12H_2O$ separates in prismatic crystals; the thallous salt $Tl_6Th(CO_3)_5$ is precipitated as a crystalline powder on adding a soluble thallous salt to a solution of ammonium thorium carbonate (Cleve, *l.c.*; *cf.* Zeitsch. anorg. Chem. 1903, 35, 424).

Thorium formate $Th(HCO_2)_4,3H_2O$ and **thorium acetate** $Th(CH_3{\cdot}CO_2)_4$, crystallising respectively in leaflets and needles, are produced by dissolving thoria in the corresponding acids; interaction between thorium salts and soluble formates and acetates leads to basic salts $Th(OH)_2(HCO_2)_2$ and $Th(OH)_2(CH_3{\cdot}CO_2)_2,H_2O$ (Haber, Monatsh. 1897, 18, 687).

Thorium oxalate $Th(C_2O_4)_2,6H_2O$ is precipitated completely by adding oxalic acid to thorium solutions even in the presence of considerable proportions of mineral acid (Brauner, Chem. Soc. Trans. 1898, 73, 951). Complex oxalates such as $K_4Th(C_2O_4)_4,4H_2O$ and $Na_4Th(C_2O_4)_4,6H_2O$ are produced by dissolving thorium oxalate in concentrated solutions of alkali oxalates (Cleve, *l.c.*; and Brauner, *l.c.*).

Thorium acetylacetonate $Th[CH(CO{\cdot}CH_3)_2]_4$, m.p. 171°, soluble in alcohol or chloroform, is prepared by adding acetylacetone dissolved in aqueous ammonia to 13 p.c. thorium nitrate solution. This salt can be distilled *in vacuô* (Urbain, Bull. Soc. chim. 1896, [iii.] 15, 1338; Biltz, Annalen, 1904, 331, 334; Zeitsch. anorg. Chem. 1904, 40, 218).

Thorium tartrates and **complex tartrates**, *v.* Cleve, *l.c.*; Haber, *l.c.*; Rosenheim, Zeitsch. anorg. Chem. 1903, 35, 424.

Thorium salts of other organic acids, *v.* Morgan, Pharm. J. 1904, [iv.] 19, 472; and Karl, Ber. 1910, 43, 2068.

Thorium oleate has been employed therapeutically in ointment form for carbuncles and other skin troubles (Martindale, Extra Pharmacopœia).

Pharmacological action of thorium, *v.* Sollmann and Brown, Amer. J. Physiol. 1907, 18, 426.

Biological action of thorium. Elemental thorium inhibits the growth of certain microorganisms and algæ without endangering the life of higher organisms (Amphioxus, Zeitsch. Elektrochem. 1911, 17, 816; Arch. Sci. Phys. Nat. 1911, [iv.] 32, 347).

Industrial application of Thoria v. GAS MANTLES. Gas mantles are generally woven in cotton or preferably ramie fibre, but artificial silk has also been employed, and formerly the thorium-cerium solution was added to the dissolved cellulose before it was spun into thread. The present practice, however, is to impregnate the woven stocking just as in the case of ramie or cotton fibre. The rare earth nitrates may be replaced by the corresponding acetates or formates and, with artificial silk, the impregnated stocking is treated with ammonia or some volatile alkali such as hydrazine or tetraethylammonium hydroxide in order to produce within the fibres the hydroxides of thorium and cerium. Hydrogen peroxide may also be employed as the precipitant. In either case, the stockings are washed free from soluble salts (ammonium nitrate, &c.) or acid; the head is hardened with a solution of magnesium, aluminium, zirconium, glucinum or chromium salt, and the mantle 'burnt off' and 'seasoned' as in the case of the ramie fibre.

Although in most instances the optimum effect is attained by mixing the thorium and cerium salts in such proportions that the mixed oxides of the mantle consist of 99·0 p.c. of thoria and 1·0 p.c of ceria, yet owing to the yellow colour of the light produced by this amount of ceria in inverted mantles using high-pressure gas, it is customary in this form of illumination to reduce the proportion of ceria to 0·5 p.c.

A pure thoria mantle gives no emission in the visible region of the spectrum and only a slight radiation of infra-red rays of short wave length. A cerium dioxide mantle gives a maximum radiation at the extreme red end of the visible spectrum, the intensity at first diminishes in the infra-red region and then increases again for heat rays of longer wave length. In this mantle there is, on the whole, a relatively considerable loss of heat by radiation, the temperature remains comparatively low and consequently the emission of light rays is only feeble.

In the Welsbach mantle containing 0·5 p.c. to 1·5 p.c. cerium dioxide, the emission of light is selective and attains its maximum in the blue region of the spectrum. On the other hand, the heat radiation is remarkably small, except for rays of comparatively long wave length. Consequently the temperature attained by the mantle is comparable with that of the flame itself. The cerium dioxide colours the transparent ground mass of thoria so that an intense selective absorption is developed in the visible region of the spectrum and, providing that the amount of colouring oxide is small, this result is attained without any appreciable increase in the loss of heat by radiation and consequently without diminution in the intensity of illumination.

One hundred parts of thoria can hold in solid solution 6·7 parts of cerium dioxide, and as the mantle contains only about 1 p.c. of the latter oxide, it is entirely in the dissolved condition. Owing to this intimate mingling of the two oxides, a very small addition of cerium dioxide suffices to bring about the intense emission of light waves whilst the increase in heat radiation is too slight to act injuriously. If, however, the proportion of cerium is raised, the greater loss of heat by radiation leads to lowering of the mantle temperature and consequent diminution in luminosity. Cerium dioxide itself is stable in the Bunsen flame, but nevertheless the ignited mixed oxides, when treated with hydrochloric acid and potassium iodide solution liberate an amount of iodine corresponding with only a portion of the dioxide originally introduced into the mixture. This result suggests the possibility of some chemical combination between the cerium and thorium oxides which may be the chemical cause of the characteristic physical properties of the Welsbach gas-mantle (*cf.* White and Traver, J. Soc. Chem. Ind. 1902, 21, 1012; Lewes, Chem. News, 1905, 26, 62; Journ. Gas Beleuchtigung, 1903, 46, 787, 974; R. J. Meyer and Anschütz, Ber. 1907, 40, 2639).

Radio-activity of Thorium.

Thorium preparations, in general, exhibit radio-activity, yielding α-rays of similar intensity but greater penetrative power than those of uranium. The β-rays from thorium are about one-tenth as intense as those from uranium, and have less penetrating power. The γ-rays are relatively feeble but very penetrating. It has been stated that the radio-activity of thorium from monazite is due to the uranium present in this mineral, and that minerals free from uranium yield inactive thorium (Baskerville, J. Amer. Chem. Soc. 1904, 26, 1642; Zerban, Ber. 1903, 36, 3911; 1905, 38, 557). On the other hand, minerals free from radium have been found to give helium and thorium emanation (Strutt, Proc. Roy. Soc. 1905A, 76, 88, 312; 1907A, 80, 56; Hahn, Ber. 1905, 38, 3371). After allowing for uranium, a constant ratio between the radio-activity and amount of thorium was found for thorium minerals in which, probably, thorium and radiothorium are in equilibrium. In thorium salts, where the radiothorium is largely removed, this constancy does not exist. Boltwood has not succeeded in obtaining inactive thorium (Amer. J. Sci. 1906, 21, 415, and 433).

Thorium hydroxide precipitated by ammonia from a solution of a thorium salt has no emanating power and only a greatly diminished α-radiation. The filtrate retains the whole of the emanating power, and the minute residue obtained on evaporation and ignition possesses the radio-activity which the precipitate has lost. The emanating power and radio-activity of this product, thorium X, disappear in the course of a month, decaying to half their original value in four days. The precipitated thorium hydroxide recovers the properties just as fast as they disappear from thorium X, and a second treatment of its acid solution by ammonia after one month leads to the separation of another quantity of thorium X having the same activity as the first fraction. Thorium X, a short-lived radioactive product of thorium, produces gaseous thorium emanation, and this in turn gives thorium 'active deposit,' which imparts radioactivity ('induced activity') to solid objects brought into contact with this disintegration product (Rutherford and Soddy, Chem. Soc. Trans. 1902, 81, 321, 837; Phil. Mag. 1902, 4, 370, 569).

Owing to the complicated nature of the disintegration changes the radio-activity of a thorium preparation is a complex function of its age. The sequence of these changes is indicated in the annexed diagram.

Mesothorium 1 is separated from thorianite by adding 26 grms. of barium nitrate to 1·5 litres of a slightly acid solution of 600 grms. of the mineral in nitric acid and by shaking the solution for an hour with excess of sulphuric acid when the sulphate of mesothorium 1 is coprecipitated with barium sulphate. The radioactive precipitate is reduced to sulphide by heating with sugar carbon in a quartz crucible and the product dissolved in hydrochloric acid. The lead is precipitated from this solution by hydrogen sulphide and traces of iron and thorium by ammonia. The radio-active chloride in the filtrate is crystallised out fractionally when mesothorium 1 is concentrated in the least soluble portions (Hahn, Ber. 1907, 40, 1462, 3304).

From monazite sand, mesothorium 1 is isolated by adding 0·1 p.c. of barium carbonate and heating the sand (400 grms.) with 800 grms. of concentrated sulphuric acid. The product is thoroughly mixed with cold water when the sediment contains practically the whole of the mesothorium 1 and radium. These two active components are concentrated from the barium sulphate precipitate by converting this product successively into sulphide and chloride, and fractionating the latter from water when the mesothorium 1 accumulates in the least soluble crystals (Soddy, Eng. Pat. 25504, 1910; Chem. Soc. Trans. 1911, 99, 75).

Mesothorium 1 is chemically identical with radium, and cannot be separated from it by fractional crystallisation of active barium chloride or other salts. On account of this complete similarity of chemical properties all radium compounds separated from uranium minerals containing thorium contain mesothorium 1, and all mesothorium preparations include the radium present in the thorium minerals, about 25 p.c. of radium being present in technically prepared mesothorium 1 (Hahn, Chem. Zeit. 1911, 35, 845).

Mesothorium 1 is rayless, and it disintegrates into mesothorium 2; its period of average life is 7-9 years, the period of half-change being 5·5 years. It behaves like a metal of the alkali earths.

Mesothorium 2 reacts like a metal of the rare-earth series, and accordingly ammonia serves to precipitate it from solutions of mesothorium 1, a trace of zirconium salt being generally added to serve as a nucleus for precipitation (Hahn, Zeitsch. physikal. Chem. 1908, 9, 246; Russell and Soddy, Phil. Mag. 1911, [vi.] 21, 130). Two other disintegration products, radio-thorium and thorium X, are co-precipitated, but if the precipitation is repeated on the solution after one or two days the second precipitate will contain mesothorium 2. relatively free from radio-thorium. Mesothorium 2 has an average life period of 8·9 hours, the half-change period being 6·2 hours; it gives β- and γ-rays; the former are heterogeneous, the absorption coefficient increasing as absorption proceeds; the γ-rays resemble those of uranium X.

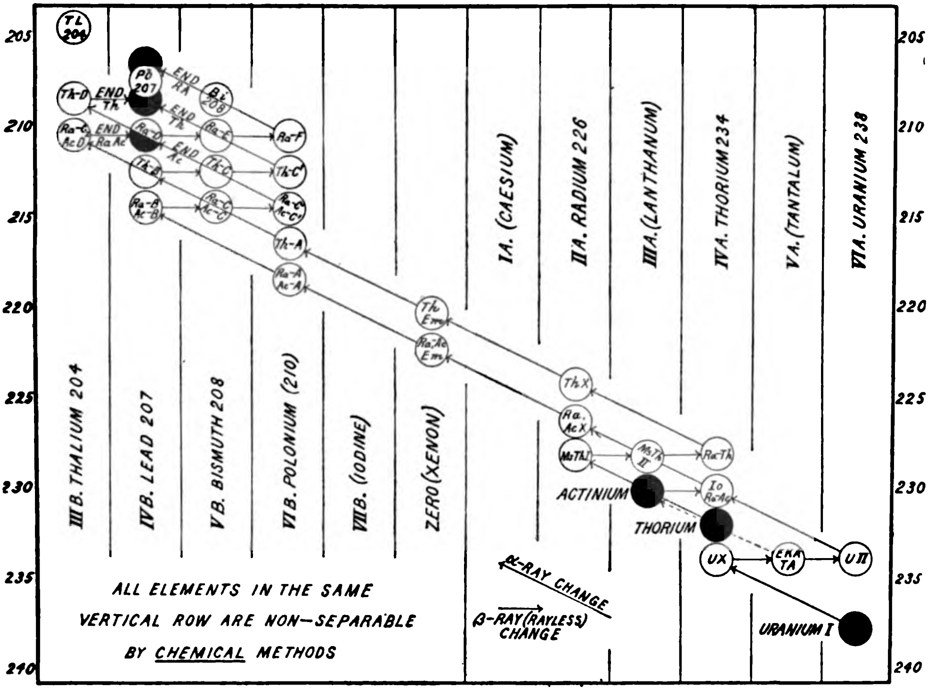


Fig. 1.

Radio-thorium. Period of average life 1063 days (?), period of half-change 737 days (?). Is chemically identical with thorium, and is only distinguished from the latter by preparing it through mesothorium 1 and 2. Mesothorium 1 is readily separated from thorium, and when left to itself produces radio-thorium, which is separated by precipitating a solution of the two disintegration products with ammonia in the presence of a trace of zirconium salt. When first precipitated in this way the radio-thorium will contain mesothorium 2, but this decays completely in the course of 3 days, while the formation of the next disintegration product, thorium X, causes an increase in the radioactivity of the preparation over a period of 3-4 weeks. The emanating power increases with the growth of thorium X, but after a month the total activity and emanating power decay to zero.

Radio-thorium preparations, especially when kept moist, are very suitable for demonstrating the properties of the thorium emanation. When the air in the tube containing a radio-thorium compound is blown between two darkened zinc sulphide screens with films turned inward, a brilliant luminescence is observed, and the decay and reproduction of the emanation can be thus illustrated (*cf.* Hahn, Ber. 1905, 38, 3371; Zeitsch. physikal. Chem. 1905, 51, 717; Phil. Mag. 1906, [vi.] 11, 793; Elster and Geitel, Chem. Zentr. 1906, ii. 302).

Radio-thorium emits α-rays which have a range of 3·9 cm. of air (Leslie, Le Radium, 1911, 8, 356).

Thorium X. Period of average life 5·35 days, period of half-change 3·7 days. Resembles radium, mesothorium 1, and the metals of the alkaline earths and remains in solution when thorium is precipitated with ammonia. The residue left on evaporating the filtrate gives on ignition a small amount of an intensely radioactive product, this activity being due to thorium X. If, however, thorium is precipitated by a carbonate or phosphate, thorium X is also rendered insoluble; the precipitate retains the initial radio-activity of the thorium compound, and when dissolved it exhibits the initial emanating power. The emanating power of a thorium solution is a measure of the amount of thorium X present (Zeitsch. anorg. Chem. 1909, 61, 338; 63, 197).

When fumaric or *m*-nitrobenzoic acid or pyridine is used to precipitate thorium both thorium X and thorium B are left in solution. In this way thorium hydroxide is freed from thorium X and its disintegration products. Four precipitations with *m*-nitrobenzoic acid give thorium hydroxide, having neither β-activity nor emanating power and a minimum of α-activity; the activity of this preparation then increases regularly without the initial decay characteristic of the precipitate obtained by ammonia (Schlundt and Moore, J. Phys. Chem. 1905, 9, 682).

Thorium X is more electro-positive than its successive products and cannot be separated from acid solutions by electrolysis or by the action of metals, only the thorium 'active deposit' being deposited. From alkaline solutions, however, all the active substances may be deposited electrolytically (von Lerch, Monatsh. 1905, 26, 899).

Thorium X exhibits an α-activity, the rays having a range of 5·7 cm. of air; it also emits feebly penetrating β-rays of low velocity, and in this respect differs from thorium and radiothorium (Levin, Phil. Mag. 1906, [vi.] 12, 177).

Thorium emanation, period of average life 76 seconds, period of half-change, 53 seconds, radio-active constant 0·0131 (sec.)$^{-1}$, α-activity, range of α-rays 5·5 cm. of air. This emanation, which differs from radium emanation in its short period and resembles it in showing α-activity, is most conveniently obtained from moist radio-thorium preparations; it is absorbed by charcoal at the ordinary temperature and is condensed on cooling, condensation starting at −120°, and being complete at −155°. The molecular weight determined by effusion is between 200 and 210, the coefficient of diffusion being about 0·1 (Leslie, Compt. rend. 1911, 153, 328). Thorium emanation, like radium emanation (niton) and actinium-emanation, belongs to the family of inert gases and is not absorbed or affected by chemical reagents. The induced radio-activity imparted to solid objects by thorium emanation lasts a few days, whilst that from radium or actinium emanation decays completely in a few hours (Rutherford, Phil. Mag. 1900, [v.] 49, 161).

Solid thorium nitrate and oxide have a lower emanating power than the hydroxide or carbonate, and in the latter case this phase of activity is further reduced by ignition. In these instances the molecules of emanation diffuse so slowly from the solid that the majority disintegrate within the substance and never escape. But when the thorium compounds are dissolved their solutions exhibit the same emanating power.

The amount of thorium present in a mineral may be quickly estimated by passing a steady current of air through the thorium solution and comparing the constant leak in an electroscope produced by the stream of emanation with that brought about by a similar volume of a standard solution of thorium mineral (*cf.* Ramsay, J. Chim. Phys. 1905, [iii.] 617).

Thorium active deposit (thorium A, B, C_1, C_2, D, and E).

	ThA	ThB	ThC_1 & ThC_2	ThD
Period of average life	0·203 sec.	15·3 hrs.	79 mins.	4·5 mins.
„ half-change	0·014 „	10·6 „	55 „	3·1 „
Radiation	α-rays	β-rays	2 α-rays	β- & γ-rays
Ranges of α-rays	—	—	5·0 and 8·6 cm. of air	—
Penetration power of β-rays (mm. of Al, half absorption)	—	0·05		0·441
„ „ γ-rays (cm. of lead, half absorption)	—		—	1·5

Thorium A, the first product of thorium emanation, is very short-lived, but its existence is indicated by the appearance of the double scintillations on the zinc sulphide screen produced by the pair of α-particles emitted by the emanation. A distinct although very short time interval separates the two members of the pair (Rutherford and Geiger, Phil. Mag. 1911, [vi.] 22, 201, 621; Zeitsch. physikal. Chem. 1910, 11, 7; Moseley and Fajans, Phil. Mag. 1911, [vi.] 22, 69).

Thorium B, the second product of thorium emanation, is practically rayless except for a feeble β-activity. Consequently, a negatively charged wire exposed for a short time to a powerful source of emanation (*e.g.* radio-thorium) has no very appreciable activity one second after withdrawal, but after a few hours acquires a powerful activity due to thorium C_1 and C_2.

On heating the active wire to red heat thorium B distils off without any appreciable effect on the activity of the wire. The inactive sublimate (thorium B) acquires an activity which, after reaching a maximum in 4 hours, decays with a half period of 10·6 hours (Phil. Mag. 1905, [vi.] 9, 628).

Thorium C is removed from a solution of thorium active deposit by absorption with animal charcoal when thorium B remains dissolved. Thorium C is also deposited alone when the solution is electrolysed or shaken up with metallic nickel. Zinc, however, deposits both thorium B and C, but not thorium X.

Thorium C gives two sets of α-rays having different ranges, these being attributed to the presence in this active product of the two constituents **thorium C_1** and **thorium C_2**; these products have not, however, been separated, and it is not known whether the two sets of rays are due to successive or concurrent changes (Hahn, Phil. Mag. 1906, [vi.] 11, 793; Ber. D. physikal. Ges. 1909, 11, 55).

Thorium D. When the thorium active deposit coating a plate or wire is kept in a vacuum at the ordinary temperature, the powerful α-ray disintegrations of thorium C_1 and C_2, one of which is the strongest known, cause a considerable proportion of thorium D to 'recoil,' *i.e.* to become projected from the plate or wire on to surrounding surfaces of the vacuous space, these receiving surfaces being kept negatively charged.

According to von Lerch's rule the disintegration of radio-active elements is accompanied by a regular increase in the electro-negative character of the successive products. But to this rule thorium D is an exception, as it dissolves more readily in acids than the other products, and is moreover more volatile than its generators, being completely volatilised from an active wire placed for 30 seconds in a Bunsen flame (Sitzungsber. Akad. Wiss. Wien, 1907, 116, [iia], 1443; 1909, 118 [iia], 1575; Zeitsch. physikal. Chem. 1911, 12, 273, 378).

Thorium D, which emits only β- and γ-rays, is the last active member of the series; its decay is regular and complete, and the nature of the ultimate product (*thorium E*) has not been completely elucidated, but this final member of the series is regarded by Soddy as an element indistinguishable from ordinary lead. Thorium D is probably non-separable by chemical methods from thallium, and like this element is coprecipitated with potassium platinichloride (Chem. News, 1913, 107, 97). Barratt has found that thorium C undergoes dual disintegration into *thorium C′*, and thorium D (Proc. Physical Soc. 1912, 24, 112).

The relationship existing between radioactive elements and the ordinary elements of the periodic classification is illustrated by the diagram on p. 481, in which can be seen the connection between the degradation products of thorium and the elements non-separable from these products by ordinary processes (Soddy, *loc. cit.*)

Bibliography.—Koppel, Die Chemie des Thoriums; Abegg, Handbuch der anorganischen Chemie, vol. iii. part 2; Böhm, Die Darstellung der seltenen Erden; Wyrouboff and Verneuil, La Chimie des Terres rares; Truchat, Les Terres rares; Rutherford, Radioactivity; Soddy, The Chemistry of the Radio-elements, 1911. G. T. M.

THORN APPLE *v.* DATURA.

THORTVEITITE. A silicate of scandium with yttrium, dysprosium, and erbium

$$(Sc,Y)_2O_3{\cdot}2SiO_2,$$

forming long prismatic (orthorhombic) crystals of a greyish-green colour and somewhat resembling epidote in appearance. It occurs in some quantity in pegmatite near Iveland in Sætersdalen, Norway, and is remarkable in being the only mineral containing scandium (Sc_2O_3 about 37 p.c.) as an essential constituent (J. Schetelig, Centr. Min. 1911, 721). L. J. S.

THSING-HOA-LIAO. A Chinese name for a cobaltiferous aluminium silicate used in the manufacture of porcelain; also applied to a cobaltiferous manganese ore used for producing a blue colour on porcelain.

THUJONE *v.* KETONES.

THULIUM. Sym. Tm. At.wt. 168·5. The erbium sub-group of the yttrium metals contains the three elements, erbium, dysprosium, and thulium; the compounds of the last of which have been hitherto studied only by few workers owing to difficulties of isolation.

Occurrence. Thulium is a very rare element, the best sources being euxenite, sipylite (a columbite from Northern Norway), ytterspar (Norwegian xenotime) and samarskite. It occurs in small quantities in the yttrium earths from other rare minerals.

Separation. Cleve first indicated the existence of the rare earth, *thulia* (Compt. rend. 1879, 89, 478, 521, 708; Thalén, *ibid.* 1880, 91, 376), and Lecoq de Boisbaudran, by decomposing fractionally the nitrates of the yttrium group, discovered thulium fractions between those of erbium and ytterbium (Compt. rend. 1879, 89, 516). A separation of erbium and thulium has been effected by fractional crystallisation of the ethyl-sulphates (Urbain, Ann. Chim. Phys. 1900, [vii.] 19, 184).

The minerals containing thulium are decomposed by hydrochloric or sulphuric acid; the rare earth oxalates precipitated, ignited, and the resulting oxides converted successively into oxalates and sulphates. The latter salts are heated with barium bromate in aqueous solution from which the rare earth bromates are fractionally crystallised. After 15,000 operations the absorption spectrum underwent no change.

Thulium bromate $Tm(BrO_3)_3,9H_2O$, hexagonal prisms, which has been obtained in considerable amount by repeated crystallisation of the more soluble portions of the rare earth bromates, is more soluble than erbium bromate, but less soluble than ytterbium bromate. Fractional crystallisation of the bromates of the yttrium earths gives a fairly rapid separation of thulium from its associates (C. James, Chem. News, 1908, 97, 61; 1911, 104, 73; J. Amer. Chem. Soc. 1910, 32, 517; 1911, 33, 1332).

Thulium salts are pale bluish-green, but their colour is readily masked by small quantities of erbium, the hue changing to yellowish-green, yellow, white, and finally pink as the amount of this impurity increases.

Thulium oxide (*thulia*), Tm_2O_3, a dense white powder with a greenish tinge, is prepared by igniting the oxalate; it is the least basic of the oxides of the erbium subgroup and dissolves slowly in strong acids. It exhibits a reddish incandescence on heating.

Thulium hydroxide is a white precipitate filtering readily even in the cold.

Thulium chloride $TmCl_3,7H_2O$, deliquescent crystals very soluble in alcohol or water.

Thulium sulphate $Tm_2(SO_4)_3,8H_2O$ is precipitated by alcohol from an aqueous solution of thulium chloride and sulphuric acid.

Thulium nitrate $Tm(NO_3)_3,4H_2O$, deliquescent crystals obtained from solution in strong nitric acid.

Thulium oxalate $Tm_2(C_2O_4)_3,6H_2O$, a greenish-white precipitate, soluble in aqueous alkali oxalates to form double oxalates.

Thulium acetylacetonate

$$Tm[CH(CO{\cdot}CH_3)_2]_3,H_2O$$

crystallises from an alcoholic solution of thulium hydroxide in acetylacetone; the absorption spectrum of this compound differs appreciably from that of the inorganic salts, nitrates, chlorides, &c.

Absorption spectrum, v. Cleve, *l.c.* and Forsling, Bit. Sv. Vet. Akad. Handl. 1899, 24, 1, No. 7). G. T. M.

THUYA OCCIDENTALIS (Linn.). In 1858 Rochleder and Kawalier (Wien. akad. Ber. 29, 10) isolated from the green portions of the *Thuya* (*Thuja*) *occidentalis* a glucoside *Thujin*, which, when hydrolysed, gave a yellow colouring matter *thujetin*. It is very probable that this compound is a member of the flavonol group.

Thujin $C_{20}H_{22}O_{12}$. The plant was extracted with alcohol, the extract when cold filtered from wax, and evaporated to a small bulk. The residue was diluted with water, and then with a few drops of lead acetate solution, the precipitated impurities removed, and the clear brown filtrate treated with lead acetate. The yellow lead compound was collected, extracted with dilute acetic acid, and basic lead acetate now added to the solution. The bright yellow precipitate was suspended in water, decomposed with sulphuretted hydrogen, the lead sulphide removed, the filtrate treated with carbon dioxide in order to free it from sulphuretted hydrogen and evaporated *in vacuô* over sulphuric acid. Crystals gradually separated, and these were crystallised repeatedly from dilute alcohol until when treated with ammonia a green coloration was no longer produced.

Thujin forms citron yellow microscopic prisms sparingly soluble in cold water. The alcoholic solution becomes yellow on treatment with alkalis, whereas with ferric chloride a dark green coloration is produced. When thujin is digested in alcoholic solution with dilute hydrochloric or sulphuric acid it is hydrolysed with formation of glucose and *thujigenin*. Thujigenin is apparently an intermediate product, which readily takes up a molecule of water, with formation of thujetin

$$C_{20}H_{22}O_{12}+H_2O=\underset{\text{Thujigenin}}{C_{14}H_{12}O_7}+C_6H_{12}O_6$$

$$\underset{\text{Thujigenin}}{C_{14}H_{12}O_7}+H_2O=\underset{\text{Thujetin}}{C_{14}H_{14}O_8}.$$

Thujetin $C_{14}H_{14}O_8$ forms yellow crystals, and is characterised by the fact that its alcoholic solution is coloured blue-green with ammonia, and green coloured by potassium hydroxide solution.

With lead acetate it gives a deep-red precipitate. When thujetin is digested with boiling baryta water it is converted into *thujetinic acid* $C_{25}H_{22}O_{13}$, which consists of yellow microscopic needles, sparingly soluble in water, readily soluble in alcohol.

Thujigenin $C_{14}H_{12}O_7$ is obtained as fine yellow needles soluble in alcoholic ammonia with a blue-green coloration, and appears to closely resemble thujetin.

The quantity of thujin which is present in the plant is very small; thus, from 240 lbs. Rochleder and Kawalier were successful in isolating a few grams only. Perkin (Chem. Soc. Trans. 1899, 829), who obtained only a trace of thujetin from 500 grms. of the material, considers that this compound may prove to be identical with myricetin. A. G. P.

THYME CAMPHOR v. Camphor.

THYME OIL v. Oils, essential.

THYMINE v. Pyrimidines.

THYMOL v. Camphors; also Phenol and its homologues.

THYMOLOFORM v. Synthetic drugs.

THYROIODINE, THYREOIDIN, THYRADEN, THYRADOL, THYREOIDECTIN v. Synthetic drugs.

TIERS ARGENT v. Aluminium.

TIGER EYE v. Crocidolite.

TIGLIC ACID v. Oils, Fixed, and Fats.

TIGLIC ALDEHYDE, TIGLIC ANHYDRIDE v. *Guaiacum*, art. Resins.

TIL or **TEEL OIL** v. Sesame oil.

TILE ORE v. Cuprite.

TIMA. A medicinal preparation imported from Tampico as a remedy for phthisis. Is prepared as a syrup by boiling the fruit of *Parmenteria edulis* (DC.) with sugar, and mixing the product with almond oil (Arch. Pharm. [iii.] 107, 375).

TIMBO. The name of a narcotic medicine, the root rind of a variety of *Conchocarpus*. The rind appears in the form of tubes or rolls, is bright reddish-brown on the outside and yellowish on the inside. The outer and middle rind break off short, but the inner rind has a long fibrous fracture and the interior colour is whitish. It possesses a weak aromatic taste somewhat like cascarilla bark, but has no special odour. A cross-section shows an interrupted yellow zone near the outer side, whilst the inner rind is faintly streaked in radiating lines. Some of the cells contain crystals of calcium oxalate (Chem. Zeit. 11, 315; J. Soc. Chem. Ind. 6, 560).

TINCAL v. Borax.

TIN MORDANTS v. Dyeing.

TIN. Sym. Sn. At.wt. 119·0. Tin was known and prized in the earliest historic ages, for it is mentioned without comment as one of the common metals in the days of Moses (Numbers xxxi. 22), and was an important commodity in the fair at Tyre; numerous bronze instruments of very early date have also been discovered in Assyria, and, particularly by Layard, in the ruins of Nineveh. Many of these bronzes are now preserved in the British Museum. The tin so employed was obtained by the Phœnicians from Cornwall and the Scilly Isles in this country, and from the mountains of Spain, and there is no evidence of the occurrence of tin in those countries in which, in ancient times, the metal was most largely used. Pliny appears to have been familiar with tin, and states that it occurs in grains, in alluvial soil, from which it is obtained by washing. These grains, he further states, are black, and their metallic character can only be recognised by their great weight. Though tin was regarded by the ancients as one of the baser metals, its cost was greater in the days of Homer and Pliny than at present, for in the days of the latter of these writers an avoirdupois pound of tin cost 8*s*. 7½*d*. sterling, or about six times its present value. The uses of tin among the Romans were similar in many respects to those of the present day. It was chiefly employed in the form of an alloy with copper, on account of the hardness imparted to the alloy by a comparatively small proportion of tin, and some of the very earliest known bronzes agree closely in composition with those used for similar purposes at the present day. Tin was also used with lead by the Romans for the production of solder, and for tinning the inside of copper and brass vessels, in which art the Roman workmen appear to have attained considerable skill. Alloys containing more tin, corresponding somewhat to the modern *speculum metal*, were used by the ancients for mirrors, but the art of tinning iron does not appear to have been discovered until a much later date.

Occurrence of tin. Tin occurs in comparatively few localities, never in the native state, and in but few forms of chemical combination. The most important ore is *tinstone* or *cassiterite*, tin dioxide (SnO_2), which is met with in two principal forms, crystallised and massive. The crystals are of the regular prismatic or tetragonal system, isomorphous with those of rutile, and are frequently well formed and of large size. Tinstone in the usual or massive form is a dark reddish-brown or slaty-coloured very heavy mineral, which occurs in Cornwall in veins usually running nearly east and west, and in which the tin ore is associated with arsenical pyrites, copper sulphide, wolfram, and a great variety of other minerals. Tin usually occurs in plutonic or metamorphic rocks, such as granite, felspar, porphyry, or clay slate, but by the action of denudation on these older rocks grains of tinstone are frequently met with in the neighbouring alluvial deposits, and this variety of ore, which is of special purity and now almost entirely exhausted in this country, is known as 'stream tin.' The metal also occurs in small quantities as *tin pyrites* (SnS_2). The largest quantities of tin are now produced in the island of Banca ('Straits tin'). Smaller though considerable quantities are met with in Britain, Germany, Austria, Siberia, China, South Australia, New South Wales, and Bolivia. Among the newer sources of tin may be mentioned the Waterberg district, to the north of Pretoria, in the Transvaal, the present monthly output of which is valued at about £30,000, and is likely to increase. Promising reports are received in connection with tin mining in Texas. In parts of Nigeria tin occurs distributed over wide areas, but in relatively small proportions. The present world's output of tin is about 115,000 tons per annum.

Production of tin. The metallurgy of tin is in its main features simple, but the mechanical preparation of the ore involves more skill and labour than is the case with any of the other common metals. So much, in fact, is this true that success in the extraction of tin frequently depends more upon the captain of the mine, who superintends the dressing of the ores, than upon the smelter. On account of the high price of tin, and the relatively high density of tinstone, it is found practicable to work ores which in the first place contain comparatively little tin, ores which contain only 0·5 p.c. of tinstone being sometimes profitably worked. The principle adopted in the mechanical separation of tinstone is very simply illustrated in the operation of 'vanning,' which is frequently used in Cornwall and elsewhere as an approximate test of the richness of an ore. A quantity of the crushed material is placed in a miner's shovel of special shape, known as a vanning shovel, water is added, and then by means of a circular motion which is imparted to the shovel by the hands, aided by a peculiar jerk of the wrist, the ore is ultimately almost completely separated from the earthy matter, and can be dried and weighed. On the large scale the ore is first picked and assorted, and then broken by suitable stone breakers and rolls. The roughly-powdered ore is carefully assorted, and then fed into a mill containing a battery of stamps, of which there are many varieties in use. Each stamp weighs 3 cwts. or upwards, the face of the stamp being either steel or chilled cast iron. By means of suitable cams on a revolving wheel the stamp is raised at regular intervals, and allowed to fall upon the ore which is contained in the box or coffer of the stamp. A supply of water flows through the boxes and escapes through perforations, carrying away the finely-crushed ore, while the larger pieces remain in the box to be further crushed by the stamp. The finely-powdered ore now passes to some form of buddle, or to a concentrating table, which more or less completely separates the earthy matter. Probably the simplest form of such apparatus, of which there is an endless variety, is the inclined plane with ridges or 'riffles' placed at right angles to its length. On such a plane the heavier particles naturally remain, the richer fragments being deposited principally at the upper part of the buddle, whilst the earthy matter, with some ore, passes away. But such a simple form of buddle is now seldom used, and a considerable number of improvements have been from time to time adopted. Thus the inclined plane is made movable, and either a jerking or a rocking motion is imparted to it, and this is found to give better results than the fixed form. But buddles of a circular shape have met with considerable favour in late years, one form (Borlase's) being a circular concave buddle fed from the outside and discharging the slimes from the middle; but the variety generally preferred in Cornwall is that of a very flat cone, the water and ore being distributed either by a revolving spout, near the apex of the cone, or by means of a smaller and more acute distributing cone. The waste liquid from the buddle is led into a succession of tanks or pools, where it is allowed to settle in order to recover the finer portion of the ore, which would otherwise be lost, and the slimes thus obtained are worked over again in order to recover the finely-divided tin ores.

In dressing tin ores it is important that they should not be too finely crushed, or the gangue will be removed with greater difficulty. The ore should be, as far as possible, separated into parcels, the fragments in each being of uniform size, and the method of treatment is varied with the fineness of the material; in no case should the ore be crushed more than is necessary to separate the matrix. These facts form the basis of all successful ore dressing.

Reduction of tin. From the point of view of the tin smelter, ores of tin may be divided into two classes, first those of tolerable purity, which may be directly smelted in the furnace, and secondly a less important class of ores, which, from the fact that they contain notable proportions of copper, arsenic, sulphur, or tungsten, require to be further treated, after dressing, before smelting. Ores which contain arsenic or sulphur are roasted at a low temperature, usually in calciners with a bed which is mechanically rotated in a horizontal plane, and which is supplied with mechanical rabbles. The greater part of the arsenic and sulphur is thus removed. The mass is then withdrawn, and, after being exposed for some time to the action of the atmosphere, is washed to remove the oxide of iron and other lighter matters from the heavy oxide of tin. Ores which contain much tungsten are heated with sodium sulphate or carbonate in a reverberatory furnace, by which means soluble sodium tungstate is produced, and can be removed by washing from the unaltered oxide of tin. This process (Oxland's) is not carried on now to any considerable extent. The ore having been purified by one or other of these processes is ready for smelting in the ordinary way. The reduction of the metal from the ore is always accomplished by heating with carbon, which operation may be performed either in a reverberatory furnace, as is the custom in this country, or in small blast furnaces such as are used to a limited extent in Germany. Shaft furnaces also are used in China, Sumatra, Nigeria, and by natives in many other localities.

Tin smelting in England. The furnace employed for the smelting of tin in this country, and in fact pretty generally elsewhere, is a reverberatory, with a fireplace at one end and a stack at the other. At the front is a single working door, while at the back is a tapping hole which is closed during the smelting, but which when the operation is concluded serves to convey the metal into a 'float' or circular iron pot lined with clay. The bed of the furnace is about 18 ft. long by 9 ft. broad, and slopes to the tapping hole. The fireplace is about 2 ft. broad, and the firebridge is of firebrick and some 14 ins. high. The roof is low, and slopes uniformly from the firebridge to the stack.

The charge of ore, which weighs 20–25 cwts., is mixed with rather less than one-fifth of its weight of anthracite powder, and spread uniformly over the furnace bottom. If the ore is refractory, a little fluorspar or lime is added as a flux. The door is then closed and luted up, and the temperature gradually raised for 5–6 hours, when the door is opened, the mass rabbled, and a quantity of powdered anthracite or 'culm' is thrown on the surface of the charge. After heating for about another hour, and a further rabbling, the metal is tapped. Part of the slag produced is thick and is raked out of the furnace, while the remainder is more fluid, flowing out with the metal, and is called 'glass' by the smelter. The slag consists essentially of ferrous silicate, and as it frequently contains a considerable amount of tin it is melted again when the furnace is at liberty.

Small blast furnaces, which were previously used in Cornwall, have survived longer in southern Germany, and are also employed by the natives of India. The waste of metal is much greater than in the reverberatory furnace, whilst the cost of fuel (charcoal) is also greater than in England, but the tin obtained is stated to be of excellent quality.

Refining. The refining process consists of two parts, a preliminary liquation, and the refining proper. The liquation is conducted in a furnace of similar shape to the reverberatory furnace above described, and about 18 tons are operated upon at once. The temperature is carefully regulated so as to just melt the purer tin, which gradually flows away into a separate pot or 'kettle,' while the impurities, consisting of iron, arsenic, sulphur, and traces of many other elements, together with some 20 p.c. of tin, remain in the form of a hard, brittle, white, semi-metallic mass known as *hard-head.* For the composition and properties of hard-head, *see* Levy and Ewen, Trans. Inst. Ming. & Metallurgy, 1908–9, 466. The purer metal which has collected in the kettle (which is heated by a small separate fire) is now refined by plunging billets of green wood under the surface of the melted tin. A quantity of gas is evolved from the wood, and violently agitates the metal, gradually separating a scum which contains the impurities originally present in the crude tin. The same result is sometimes attained by 'tossing' the melted metal in ladles from a height of several feet and allowing it to fall into the kettle; in this way the metal is also exposed to atmospheric influences, and a scum separates as before. The refined metal is sold as *grain, refined,* or *common tin,* according to its quality, though all tin met with in commerce has been more or less refined. For *refined tin* purer ores are employed, the refining is continued longer, and after poling the metal is allowed to stand some time, and only the upper or purer portions are used. The second or ordinary quality, when cast in suitable moulds, is known as *block tin.* A simple test of the commercial quality of tin is to melt the metal at a moderate temperature, and to pour it into an ingot mould. The ingot, if of good quality, should be smooth, bright, and rounded, and should retain this appearance on solidification; if impure it will have more or less sharp edges, and will 'frost' over on solidifying, while very impure metal will be tinged with yellow or purple, according to the amount and nature of the impurities. *Grain tin* is produced by heating blocks of refined tin to a temperature a little below the melting-point of the metal, at which point it becomes very brittle, and is broken either by dropping from a height or by a blow of a hammer. For further particulars of the properties and metallurgy of tin, *see* H. Louis, Metallurgy of Tin, London, 1911.

Brands of tin. In 1911 a committee of the London Metal Exchange drew up a new form of contract for the purchase of tin. This provided for the recognition of two classes of tin: Class A. includes Straits or Australian tin of good merchantable quality, and also refined tin of good merchantable quality, assaying not less than 99·75 p.c. of tin. Class B. includes common tin of merchantable quality, and assaying not less than 99 p.c. of tin. The official brands include the following: Straits, Australian, Banca, Billiton, English, German, and Chinese. In connection with this classification a number of brands and descriptions were assayed, and tabulated analyses prepared (p. 487).

It will thus be seen that some of the best brands of commercial tin are of remarkable chemical purity.

Uses of tin. The manufacture of tin plates absorbs more tin than any other industry, and of this a separate account will be given. Tin is also largely used for alloying with copper to produce

——	Tin	Antimony	Arsenic	Lead	Bismuth	Copper	Iron	Silver	Sulphur
Banca tin	99·950	0·007	nil	trace	nil	0·018	0·045	nil	trace
Billiton . . .	99·960	0·006	nil	nil	nil	0·023	nil	nil	nil
Penang	99·939	trace	0·013	trace	nil	0·016	0·028	nil	0·004
Singapore tin . . .	99·870	0·008	0·045	0·034	0·003	0·052	0·003	0·006	0·005
M. Bischoff . . .	99·795	0·005	0·063	0·037	0·005	0·035	0·042	trace	0·008
Pyrmont tin . . .	99·938	0·017	0·019	trace	nil	0·022	trace	nil	0·004
Irvine Bank . . .	99·580	0·062	0·034	0·221	0·025	0·125	0·002	0·018	0·004
Williams Harvey & Co., No. 1	99·860	0·015	0·040	0·004	0·005	0·047	0·003	nil	0·006
,, ,, No. 2	99·560	0·166	0·037	0·162	0·007	0·050	0·005	trace	0·013
,, ,, No. 2*a*	99·350	0·245	0·065	0·223	0·015	0·042	0·016	trace	0·013
,, ,, No. 3	99·200	0·300	0·037	0·396	0·007	0·100	0·013	0·014	0·006
,, ,, No. 4	99·941	0·011	0·022	trace	0·001	0·020	trace	trace	0·005
Penpoll, No. 1 . . .	99·720	0·118	0·054	0·041	0·007	0·052	0·001	0·009	0·007
,, No. 2 . . .	98·710	0·569	0·042	0·546	0·055	0·103	0·007	0·015	0·004
,, No. 3 . . .	99·300	0·325	0·056	0·212	0·050	0·088	0·002	0·021	0·009
Redruth	99·160	0·178	0·053	0·177	0·017	0·445	0·014	0·006	0·008
Th. Goldschmidt, No. 1 .	99·860	0·004	nil	0·102	nil	0·043	trace	nil	trace
,, No. 2 .	99·460	0·015	nil	0·425	nil	0·069	trace	nil	trace
,, No. 3 .	99·150	0·122	0·046	0·143	0·112	0·352	0·007	0·003	trace
Chinese, No. 1 . . .	99·343	0·031	0·040	0·434	0·007	0·052	0·010	trace	0·011
Wing Hong & Co., No. 2 .	98·662	0·039	0·035	1·035	0·012	0·134	0·014	trace	0·011
,, ,, No. 3 .	95·280	0·381	0·050	3·995	0·020	0·106	0·028	0·018	0·008

bronze, bell metal, and speculum metal, while in combination with other metals tin produces a number of useful alloys, to be afterwards described, among which may be mentioned pewter, Britannia metal, plumber's (or soft) solder, Queen's metal, type metal, fusible metal, &c. Though tin is comparatively brittle at ordinary temperatures, it becomes very malleable at about 100°, and can then be rolled into thin sheet or foil, for which there is a considerable application, and which was formerly much used, in the form of an amalgam, for the 'silvering' of mirrors. On account of its power of resisting atmospheric influences and the action of vegetable acids, tin is also used for the manufacture of pipes for brewers, distillers, and other purposes. For similar reasons lead pipes are sometimes tin-lined. Pots, pans, kettles, and other culinary utensils are frequently *tinned* inside. The process is very ancient, and extremely simple. The surface of the vessel to be tinned (which may be of copper, brass, or iron) is carefully cleaned and brightened, and a little ammonium chloride (patented for this purpose by John Bootie in 1768) is often rubbed over the surface. Some tin and a little powdered resin is now melted in the vessel, and is wiped over the surface with tow. By this means a skilful workman rapidly produces a uniform coating of tin, which resists considerable wear, and yet weighs, according to the experiments of Bayen, less than a milligramme per square inch of surface. No wonder that Pliny states, with surprise, that copper when tinned does not increase in weight ! Tin salts are also used for tinning brass and copper wire, and as mordants in dyeing.

Alloys of tin. The alloys of tin are of great practical importance, and have naturally attracted considerable attention, although accurate information is still wanted in respect of many of their physical and other properties. For convenience of study the alloys of tin may be divided into two classes, the first in which the properties of the resulting alloy are entirely different from the mean of the constituents, while the second class includes those alloys some of the most important properties of which agree very closely with what might be anticipated from the properties of the constituent metals. The first class is typically represented by the alloys of copper and tin, which include the important alloys known as *bronzes*, *gun metal*, *bell metal*, &c. Tin itself is weak, soft, readily fusible, and of a nearly white colour, while copper is strong, tough, moderately hard, and of a characteristic red colour. On adding tin to copper, however, in gradually increasing proportions a succession of alloys is obtained with properties which are utterly different alike from those of each other and from their constituent metals. Thus an addition of about 5 p.c. of tin to copper produces a tough strong alloy, which still retains a fairly characteristic copper colour, but which is much harder than copper, and is suitable for medals or coinage, but the hardening effect of tin is so great that already the practical limit has been reached for coinage purposes. On adding 5 p.c. more tin we have an alloy which is still harder, so much so that it has to be cast instead of being rolled or drawn, and the alloy possesses a rich yellow colour. With a little more tin an alloy suitable for the hardest bearings is produced, and with still more tin we have the alloy used for small bells, and which is sonorous, but shows considerable brittleness when cold, but which may be worked at a low red heat. With still more tin an alloy suitable for the largest bells is obtained ; brittleness is more marked, and the fracture is dull earthy grey, and it is only when the metal has been worked or burnished that a yellow colour is visible. But on continuing the addition of tin, which is one of the softest of the common metals, the alloys become more and more brittle, until with about 33 p.c. the alloy can easily be pounded in a mortar, and possesses a white colour, with a more or less pronounced blue shade. This alloy is thus utterly different alike from its constituents and from either of the other alloys previously mentioned. As examples of the second class of alloys of tin, in which the properties of the alloy are approximately what would be expected from the characters of the constituents, the combination with zinc or with lead may be taken. Tin and zinc unite in all proportions, and the colour, hardness, ductility, &c., of the alloys are what would be anticipated from a mixture of the two constituents. Tin and lead also unite in all proportions to form a series of alloys, all of which are nearly white in colour, and are soft, malleable, and readily fusible, like the metals themselves. Tin-lead alloys, however, furnish a characteristic illustration of the fact that the melting-point of mixtures or alloys is very commonly lower than the mean calculated from the melting-points of the pure substances. This rule is very generally observed, both in salt solutions, with mixtures of salts, and with mixtures of organic substances (Guthrie, Phil. Mag. [iv.] 49, 1, 206, 266; [v.] 1, 49, 354, 446; 17, 462; 6, 35). Common, or soft, solder is an alloy of tin and lead, the best proportions being very nearly 2 parts of tin to 1 of lead. The melting-point of this alloy, calculated from the melting-points of its constituents (Pb=327°, Sn=228°), would be 261°, but the lowest melting-point in this series of alloys actually observed is 180° (Turner, B'ham. Phil. Soc. [iv.] 318), and the composition of the alloy was very nearly 2 parts of tin to 1 of lead. A number of investigators have examined these alloys of tin and lead, including Küpffer, Pillichody, Laurie (Chem. Soc. Trans. 1889, 678), and more recently Rosenhain and Tucker (Phil. Trans. Series A. 1908, 89), and the results of the determination of the composition of the lowest melting-point alloy vary from about 60 to 65 p.c. of tin (62·93 p.c. tin, Rosenhain and Tucker). There appears to be no indication of a definite alloy of tin and lead in atomic proportions, though, on very slow cooling, there is evidence of the existence of a solid solution, at the lead end of the series. There is also an inversion at 150° with alloys containing 18–63 p.c. of tin. In addition to their use for solders the tin-lead alloys have an important application in the form of *pewter*, the toughest and hardest variety of which contains about 3 parts of tin to 1 of lead. Alloys of tin and antimony belong to the same class as those previously mentioned, and a mixture of 4 parts of tin with 1 of antimony is used for one kind of type metal. Tin also enters into the composition of Britannia metal, the proportions being as follows (Greenwood, Metallurgy, i. 211):—

	Britannia metal			
	For spinning	For rolling	For casting	Queen's metal
Tin . . .	94	90	84	75
Antimony . .	5	7	10	8·5
Copper . .	1	3	4	—
Bismuth . .	—	—	2	8
Lead . .	—	—	—	8·5

A Birmingham manufacturer's mixture for Britannia metals is as follows: tin, 1 cwt.; antimony, 12 lbs.; copper, ½ lb.

Britannia metal has a somewhat considerable application on account of its white colour, and the fact that it takes a good polish and resists the influence of the atmosphere; its low conductivity for heat also renders it very suitable for some purposes. This manufacture was introduced by Jessop and Hancock about 1770.

Type metal varies considerably in composition, consisting essentially of antimony and lead; but for small type tin is commonly added, and in some cases considerable proportions of tin are employed.

The following illustrates the composition of type metal of excellent quality, and suitable for different sizes of type. It will be noted that large type is made of a softer and cheaper mixture.

	Tin	Lead	Antimony
Large type . .	7·5	78	14·5
Medium type .	9·0	73	18
Small „ .	14·5	57	28·5

From 1 to 1·5 p.c. of copper is also added in some cases to improve the wear of the type.

White bearing metals for heavy machinery contain the same constituents as type metal. At least 10 p.c. of antimony is required: with above 20 p.c. the alloy is brittle. The limit of tin, on account of price, is usually about 45 p.c. (Hague, Bearing Metals, South Staffs. Iron & Steel Inst. Jan. 1909; Hiorns, Anti-friction Alloys, Birm. Metallurgical Soc. Feb. 1909). For special purposes larger proportions of tin are employed, as shown in the following analyses (G. Hughes, Non-ferrous Metals in Railway Work, Journ. Inst. of Metals, Sept. 1911)—

	A	B	C
Tin	82·0	11·5	80
Antimony . .	14·0	13·5	10
Copper . . .	4·0	3·0	10
Lead	—	72·0	—

Alloy B is a fairly typical soft bearing metal. A and C are harder, the former being used for bearings, &c., in steam locomotives, and the latter for high-class axle bearings on the pinion and commutator ends of electrical rolling stock.

Tin is also a constituent of the various *fusible alloys*, one of the best known being *Wood's* alloy, which consists of 4 parts of tin with 4 of lead, 8 of bismuth, and a little cadmium; it fuses at 63°.

The tin-lead-bismuth eutectic melts at 94°. It can be prepared by melting together 4 parts of tin, 8 of lead, and 13 of bismuth. The alloy with 4 of tin, 8 of lead, 10 of bismuth, and 4 of cadmium melts at about 71°.

Fusible alloys are used chiefly for taking rapid impressions of objects which would frequently be injured by the use of metal melting at a higher temperature, and also for safety plugs in steam boilers, &c.

Tin-copper alloys. *History.*—Copper is one of the few metals which have been known from prehistoric periods, and, like silver and gold, is in the pure condition too soft and ductile for many useful applications. The ancients, therefore, prepared various hard copper alloys or bronzes, which were used for many purposes to which iron and steel are now applied. The elements added to give hardness were arsenic, iron, or, preferably, when obtainable, tin. A very ancient Egyptian knife-blade (1400 B.C.) examined by Dr. Percy (Metallurgy, i. 504) consisted of copper with 2·29 p.c. of arsenic and 0·43 p.c. of iron; such a material would, of course, form an indifferent cutting tool.

The Hindoos have for many centuries produced a variety of bronze for coins and statues, which was hardened by the presence of iron. Dr. Percy mentions an ancient Indian coin which contained 5·06 p.c. of iron, the remainder being copper (*l.c.*), while in the Birmingham Art Gallery there is one of the earliest known images of Buddha, which is believed to be 2500 years old, and which was found by Daniel Forbes to contain 91·50 p.c. of copper and 7·59 p.c. of iron. With the introduction of tin by the Phoenicians came the use of bronze in Egypt, Assyria, Greece, and all the important countries of the ancient world. Of these bronzes, numerous examples are preserved, and the composition recommended for various purposes was very similar to that which is used at the present day. Thus Pliny states (Thomson, Hist. Chem. i. 57) that the Romans made their pans for boiling from a mixture of 100 lbs. of copper and 3–4 lbs. of tin, while for statues to every 100 lbs. of copper, consisting of one-fourth old copper and three-fourths new metal, 12½ lbs. of tin was added. Brass was not known, or at all events was not in general use, until shortly before the Christian era, and the references to brass which so frequently occur in the Old Testament have to do either with copper or bronze, and not with alloys of copper and zinc. *See* further on the early history of copper and copper alloys, W. Gowland, Presidential Address, Institute of Metals, 1912.

Constitution of copper-tin alloys. Previous to the researches of Matthiessen, it was customary to regard alloys as examples of chemical combination, and most experimenters prepared and studied alloys of definite atomic proportions. An example of this method of working is to be found in the researches of Mallet on the tin-copper alloys (Brit. Assoc. Rep. ix., Construction of Artillery, p. 82). The remarkable change in properties which results when tin and copper are alloyed was used as an argument in favour of the view that definite chemical compounds were produced. The result of more recent investigations, however, tends to show that although in some cases definite atomic combinations actually do occur, still these are comparatively few (*see* C. H. Desch, Intermetallic Compounds, Journ. Institute of Metals, vol. i. 227); while the other alloys, which constitute the vast majority of those in use, are either solid solutions of a metal in an excess of one of the constituent metals, or are simply mixtures of the two or more metals present in the alloy. The equilibrium of the copper-tin series has been studied by Heycock and Neville (Phil. Trans. 202A, 1: Giolitti and Tavanti, Gazz. chim. ital. 1908, 38, ii. 209; Shepherd and Blough, J. Phys. Chem. 1906, 10, 630; Haughton and Turner, Jour. Institute of Metals, 1911, part ii.). For a discussion of the equilibrium diagram, *see* art. **Metallography.** In the tin-copper series there is good evidence of the existence of a definite alloy Cu_3Sn containing 61·64 p.c. of copper, while there is considerable reason to believe that Cu_4Sn, containing 68·18 p.c. of copper, also exists. Thus Calvert and Johnson (Phil. Trans. 1858), in investigating the conductivity for heat of these alloys, found a maximum conductivity corresponding to Cu_3Sn, and a minimum conductivity corresponding to Cu_4Sn. Some very interesting determinations by Riche (Compt. rend. 55, 1862, and more completely Ann. Chim. Phys. [iv.] 30, 361) show two maxima, corresponding to Cu_3Sn and Cu_4Sn. These experiments have also received strong support from the induction balance curve of Roberts-Austen (Phil. Mag. 1879, [ii.] 57), which shows two distinct breaks corresponding to Cu_3Sn and Cu_4Sn. The determination of relative electric conductivity by Lodge (*ibid.* 1879, [ii.] 554) also show a very distinct maximum at Cu_3Sn and a minimum conductivity corresponding to Cu_4Sn. Laurie examined these alloys from the standpoint of the electro-motive force produced in a standard cell, and concluded that there was very definite evidence of the existence of Cu_3Sn, but failed in this way to obtain any proof of the existence of Cu_4Sn (Chem. Soc. Trans. 1888, 109; 1889, 678).

The evidence in favour of Cu_3Sn is therefore exceedingly strong, while that in favour of Cu_4Sn, though not quite so complete, is still good, and at present there is no trustworthy evidence in support of any other atomic combinations. Further evidence on this point will be found in C. H. Desch's paper on Intermetallic Compounds, Journal Institute of Metals, 1, 1909, 227, above cited. These facts, when considered in connection with the known characters of the two alloys in question, give a key to the peculiar characters of the useful tin-copper alloys. The two definite alloys are white, hard, and brittle, and practically all the alloys used in the arts, except speculum metal, contain more copper than $Cu_4Sn = 68·18$ p.c. Cu. Hence the useful bronzes may be regarded as mixtures of one of two definite alloys with an excess of a solid solution of tin in copper, and these tend to separate more or less completely during solidification. This separation is particularly marked with large castings rich in copper, as in *gun metal*, which was in former times largely used for ordnance. Microscopical examination shows clearly that at the copper rich end of the series of alloys the first constituent to separate out on cooling the fluid alloy is a solid solution of tin in copper. This forms a dendritic, or fir-tree like structure, giving cores which increase in tin from the centre outwards. This copper-rich solid solution is called the α constituent, and is relatively soft and ductile; as the proportion of tin increases harder constituents separate out, the first of them being designated by the symbol β. It is harder and more brittle than α.

The production of bronze castings requires special precautions, which cannot be described here. For details, *see* Mallet On the Construction of Artillery, 1856; also Reports of the United States Chief of Ordnance, 1880, 126, 189; 1884, 369. These latter reports contain some important observations with regard to this variety of bronze. It is stated that the best proportion for such purposes is 91 of copper to 9 of tin. This is best cast in a mould or 'chill' of cast iron, and 100 tests of metal so prepared gave an average tensile strength of 21·9 tons per square inch, the maximum being 24·8 tons and the minimum 16·5 tons. It should be mentioned that these values are higher than those usually obtained in this country, where the metal is generally cast in sand moulds.

Composition of principal tin-copper alloys. The following list is based on that given by Holtzapffel (Mechanical Manipulation, i. 270).

Tin, 0–5 p.c. A small quantity of tin is sometimes added to copper for engraver's purposes to give crispness. About 5 p.c. was used by the Romans for pans, and for ancient flexible bronze nails. A similar alloy is now used for bronze coinage and medals, often with a little of the tin replaced by zinc; also for engineers' soft gun metal or 'brasses.'

7 p.c. Slightly harder alloy; suitable for mathematical instruments, &c.

8·5 p.c. Rather harder; fit for wheels to be cut with teeth.

8–12 p.c. Soft bronze statues of the ancients. These alloys are harder than the preceding, and mark the extreme limit for coinage purposes. Also used for brass ordnance, 9 or 10 p.c. of tin being preferred. Medium engineers' 'brasses' contain 10–12 p.c. of tin.

12–14·5 p.c. Hard bronze of the ancients, used for weapons and tools. These proportions are also used for engineers' hard bearings.

16 p.c. Soft musical bells.

18–20 p.c. Chinese gongs and cymbals.

20 p.c. Small house bells; Indian gongs.

22 p.c. Large house bells.

24 p.c. Limit for large church bells.

About 33 p.c. Speculum metal (*v.* Phil. Trans. 1840, 503).

About 66 p.c. 'Temper,' an alloy used for addition to tin and lead to harden pewter.

It has already been mentioned that the addition of a small quantity of tin to copper prevents it rolling well when hot, and the addition of a little more tin destroys its malleability when cold. Bronze is tempered by an exactly opposite process to that used in the case of steel, namely, the alloy is heated to redness and then rapidly cooled in water.

For the majority of purposes bronze is melted in crucibles of fireclay or plumbago, the charge being about 90 lbs. For large castings a reverberatory furnace is often employed, though such work is sometimes performed by means of a large number of crucibles. It is recommended that the copper should be well melted and kept in fusion for some time before the tin is added, if strong castings are required. Founders also prefer to use some new metal in every charge, and not merely to re-melt scrap. The oxidation which takes place during melting removes some 3 or 4 parts of copper to 1 of tin; the result is, therefore, that the alloy, which contains about 9 parts of copper to 1 of tin, tends to get poorer in tin by remelting, and due allowance must be made for this loss, even though it may appear to be slight, as small differences in composition often exert a most important influence in tin-copper alloys.

Bronze bearing metal. According to Dudley (Jour. Franklin Inst. 133, 81, 161; J. Soc. Chem. Ind. 11, 460), the following composition is very suitable for bearings for locomotives and similar purposes: copper, 77; tin, 8; lead, 15. The presence of lead in bearings very much diminishes the loss of metal caused by wear, and also reduces the local heating of the journals. Phosphor bronze and other varieties of bearing metal for similar purposes to the above often contain about 10 p.c. of lead, and the wearing properties of the alloys is chiefly connected with the proportion of copper and tin to lead. The presence of tin is necessary in order to obtain a uniform alloy, as lead and copper alone do not unite well. With too much tin the alloy wears more rapidly and becomes more heated. The presence of phosphorus and arsenic gives solidity to the castings, but with suitable proportions of tin and lead, as above, alloys are obtained which wear even better than standard phosphor bronze with the following composition: copper, 79·7; tin, 10; lead, 9·5; phosphorus, 0·8 p.c.

Phosphor bronze is an alloy containing copper and tin in various proportions, and which also contains a small quantity of phosphorus, introduced in the form of phosphor tin. Occasionally small quantities of zinc or lead are also added. The phosphorus varies from a mere trace, added chiefly to ensure soundness in casting, to about 1·75 p.c. with hard alloys. The results of the analyses and mechanical tests of 99 samples of phosphor bronze, as received by the British Admiralty, have been given by A. Philip, Journ. Inst. of Metals, 1, 164, while the constitution and microstructure have been dealt with by O. F. Hudson and E. F. Law, Journ. Inst. of Metals, iii. 1910, 161. This alloy has met with considerable favour where special strength or power of resisting wear (as with bearings for quick running machinery) is required. Similar alloys containing manganese, which is added in the form of ferro-manganese, have also met with considerable application, and are known as *manganese bronzes. Silicon bronze,* made by the addition of copper silicide, is used for conductivity wire, though many of these so-called bronzes contain very little or no tin. They are usually alloys which closely resemble Muntz metal in composition, and contain about 60 p.c. of copper, 38 p.c. of zinc, and the remainder of specially added elements, such as manganese, and impurities. T. T.

Dry assay of tin ores. Hofman finds that Winkler's method of assaying black tin stone gives results averaging 65·96 p.c., or 1·88 p.c. too low, the figures disagreeing amongst themselves up to over 3 p.c. The process consists of reducing together 5 grms. each of cassiterite and cupric oxide with 15 grms. of black flux, 1·25 grms. of borax, and a little salt as a cover. A similar experiment is conducted without the cassiterite, and the copper obtained in the one case deducted from the alloy in the other gives the amount of tin. The following modifications of this method were tried: increasing the amount of charcoal, using chalk-lined crucibles, omitting the salt and increasing the potassium carbonate, and Rickett's modification of adding argol; but they all gave worse, and in some instances very variable, results.

The iron method—reduction with hæmatite, charcoal, and potassium cyanide or fluorspar—gave unsatisfactory results. The same may be said when a mixture of ferrocyanide and cyanide was used, and also when any of the Cornish methods were employed. So far, with fairly pure cassiterite only two methods have proved satisfactory, viz. the German and the pure cyanide methods. Hofman has attempted to prove which of these two methods gives the best results when the cassiterite is mixed with those minerals likely to be naturally associated with it. The minerals used were quartz, felspar, mica, tourmaline, garnet, and columbite. Mixtures of the purified cassiterite ore with varying proportions of each of these minerals were assayed by both methods, the percentage of tin being calculated on the cassiterite ore present. The charges were so regulated that the flux in the German assay was always equal to three times the quantity of ore *plus* the mineral, and in the cyanide assay to six times the quantity. In the latter case 4 parts of cyanide were mixed with the ore; 1 part was used to coat the crucible bottom, and 1 part as a cover. In all cases the cyanide method gave more concordant, and less prejudicially affected, results than the other. The results of the German assays fluctuated greatly as the amount of mineral present increased. Thus, in the case of quartz and albite the results were lower as the quantity of mineral was increased, the respective figures being, with 37·5 p.c. of each mineral, 60·7 and 60·2 p.c.; the corresponding cyanide figures being 63·90 and 65·30 p.c. (the real percentage of tin was 67·84). The tin buttons, moreover, in the German assay with albite contained iron, while those by the cyanide process were free, the temperature of fusion being too low to cause decomposition of the albite.

With muscovite, tourmaline, garnet, and columbite the results with the German method were very unreliable, being sometimes too high and very ferruginous, and sometimes too low, varying from 82 p.c. with 50 p.c. of garnet to 46 p.c. with 44 p.c. of tourmaline. The cyanide method gave fairly good results in all the above cases, very little iron getting into the buttons, except in the case of garnet, when the result was 69·89 p.c., with 37·5 p.c. of mineral present. With the same quantity of muscovite, tourmaline, and columbite the assays were respectively 63·3, 64·7, and 66·0 p.c. Consequently, where anything like a true result is required the cyanide assay is by far the most to be relied upon, and should be employed in cases of buying and selling, although in concentration works, where comparative results and large numbers of assays are required, the question of cost must be considered, and the cheaper German method might be adopted.

Hofman emphasises the importance of properly preparing the ore for assay, and states that the ordinary method of grinding the whole sample to a uniform size is not suited to the tin ores of the Black Hills, chiefly on account of the preponderance of mica. Hence a preliminary sizing is advantageous. The ore while being pulverised is screened through a series of sieves Nos. 20, 40, 60, and 80, the different-sized screenings being then washed. This method gives purer concentrates, and necessitates less loss of cassiterite, as the material has been washed without excessive grinding, which in the present process reduces the brittle cassiterite to a slime, while some of harder associated minerals are only converted into sand. The subsequent treatment of the concentrates mentioned in the first part of the paper is recommended, as the roasting renders the cassiterite more friable and more readily reducible, the assays in some cases showing a difference of 0·5 p.c. between the raw and roasted ores in favour of the latter (Part ii., H. O. Hofman, Technol. Quarterly, 3, 261–280; J. Soc. Chem. Ind. 9, 1154; *v.* Rennie and Derrick, *ibid.* 1892, 662).

COMPOUNDS OF TIN.

Oxides. A monoxide, *stannous oxide* SnO, and a dioxide, *stannic oxide* SnO_2, each of which gives rise to a distinct series of salts, are known, the former acting as a base and the latter acting as either base or acid. Oxides of the composition Sn_2O_4, $SnO{\cdot}3SnO_2$, $2SnO_3,H_2O,SnO_2$ and others have also been said to exist, but it is probable that, with the exception of SnO_3, they are mixtures of the other two oxides.

Stannous oxide SnO is obtained as an olive-brown anhydrous powder, when stannous oxalate is heated out of contact with the air; or as a white precipitate of the composition $2SnO,H_2O$, with evolution of carbon dioxide, when stannous chloride and an alkaline carbonate or hydroxide are mixed in solution. If the precipitate is washed with air-free water, and the lixiviated product is heated in the absence of air, nearly pure dark grey stannous oxide is obtained (Enequist, Eng. & Mining J. 1895, 219; *see* also Hantzsch, Zeitsch. anorg. Chem. 1902, 30, 289).

It may also be obtained as a bluish-black anhydrous powder by heating a mixture of 4 parts of stannous chloride with 7 of sodium carbonate, and lixiviating the resultant mixture of stannous oxide and sodium chloride (Sandall, J. pr. Chem. [i.] 254). The anhydrous oxide may also be obtained from the hydrated form as follows: (1) as a black powder by heating it out of contact with the air; (2) in minute cubes by digestion with acetic acid at 56°; (3) of a brilliant scarlet colour, which becomes brown on rubbing, by evaporating a dilute solution of ammonium chloride containing stannous chloride in solution until the chloride commences to crystallise (Fremy, Berz. J. 24, 133; 25, 172; Ann. Chim. Phys. [iii.] 12, 460); (4) as small black shining crystals, which, when heated to 258°, decrepitate and swell up, with production of soft olive-green laminæ, by prolonged digestion with a weak solution of caustic potash at the ordinary temperature (Fremy, *l.c.*). A stronger solution dissolves the oxide and ultimately deposits it in crystals, the deposit from a solution of 4 parts of potassium hydroxide in 10 of water containing potassium stannate and tin, the former produced by absorption of atmospheric oxygen. Fremy also describes various red, black, brown, and other forms of this oxide.

Stannous oxide becomes incandescent, and forms stannic oxide, when heated in the air. It is violently oxidised by nitric acid and other oxidising agents. Carbon or hydrogen reduces it to metal at a red heat. It dissolves in acids, with production of stannous salts, and in caustic potash or soda, but not in ammonia. The soda solution is employed in calico printing and dyeing under the name *sodium stannite*, and is prepared as described under *sodium stannate*.

Stannous oxide and tin salts are used as reserves under paranitranaline red and other diazo colours (Bull. Soc. Ind. Mulhouse, 1900, 45).

Stannous oxide is sometimes recommended for use in glass and enamel manufacture, but it is too costly, and the results are not very satisfactory.

A so-called *sesquioxide* Sn_2O_3 is obtained as a slimy grey precipitate by the action of recently-precipitated ferric hydroxide on a solution of stannous chloride (*v.* Fuchs, Kastner's Archiv. für Chemie und Meteorologie, 23, 368; J. pr. Chem. 5, 318; and Berzelius, Pogg. Ann. 28, 443; Berz. J. 13, 110).

This substance is readily soluble in ammonia and in concentrated hydrochloric acid. It does not appear to form definite salts. Its hydrochloric acid solution acts like a mixture of stannous and stannic chlorides. An orange-yellow oxide of the composition $SnO \cdot 3SnO_2$ is obtained by digesting metastannic acid in cold aqueous stannous chloride (Fremy, J. Pharm. [ii.] 1, 344).

Stannic oxide SnO_2 occurs as *cassiterite* or *tinstone*, varieties of which are known as *stream tin*, *wood tin*, *toad's eye*, &c. Daubrée (Ann. Mines, 20, 65) has pointed out that, with the exception of quartz, the minerals most frequently associated with tin ore are fluorine compounds.

Stannic oxide is obtained as an anhydrous white powder of sp.gr. 6·7122 at 4° (Joule and Playfair, Chem. Soc. Trans. 1849, 1, 128) when tin is heated until it burns in the air. The powder is converted into microscopic quadratic crystals resembling the native oxide when heated in a current of hydrogen chloride (Deville, Compt rend. 1861, 53, 161; *see* also Abel, Chem. Soc. Trans. 1858, 119). The oxide may also be obtained in trimetric crystals, and is therefore dimorphous (*v.* Daubrée, Pharm. Zentr. 1849, 821; Levy and Bourgeois, Compt. rend. 94, 1365).

It has also been obtained in oblong and rhombic plates of sp.gr. 7·0096 and approaching the form of anatase (Emich, Monatsh. 1893, 14, 345).

Metallic tin may be heated electrically or otherwise to 1700° out of contact with air, and the resulting tin vapour is then burnt in a current of air or oxygen. The stannic oxide thus produced is said to be more homogeneous and in a better state of subdivision for enamelling than the ordinary oxide (Eng. Pat. 9231, 1900).

Stannic oxide is obtained from its ores or from dross, waste, &c., by heating the ore or waste with or without an admixture of coke, chalk, or dolomite and acting upon the liberated molten tin with hot air or oxygen (Fr. Pats. 392805, 392806, 1908; 370640, 1906; 409157, 409485, 1909; also Eng. Pats. 12910, 1899; 28565, 1908; U.S. Pats. 695939, 1912; 780984, 1905; 880873, 1908; J. Soc. Chem. Ind. 1900, 448; *ibid.* 1905, 197; *ibid.* 1908, 335; *ibid.* 1909, 21; *ibid.* 1910, 352; *see* also *ibid.* 1904, 1239; *ibid.* 1907, 696, 1094).

The dioxide may also be formed by electrolysing a solution of sodium chloride using a tin plate as anode and a platinum plate as cathode (Lorenz, Zeitsch. anorg. Chem. 1896, 12, 436).

Stannic oxide is reduced to metal when heated with hydrogen, carbon monoxide, carbon, potassium, or sodium (Doeltz and Graumann, Metallurgie, 1907, 4, 420). It dissolves in fused potassium disulphate, but separates from the mass when treated with water. When fused with sulphur, stannic sulphide is formed, with evolution of sulphur dioxide.

The anhydrous oxide is insoluble in acids, except in concentrated sulphuric acid, with which it forms a syrup decomposed by dilution, with precipitation of the oxide. It dissolves in aqueous or fused alkalis, with formation of stannates.

Treated with hydrochloric acid in presence of tin both stannous and stannic oxides form stannous chloride, and this is used as a method for the recovery of tin from the waste liquors of the dye house (Vignon, Textile Colourist, 18, 333; J. Soc. Chem. Ind. 1893, 762).

With chloroform stannic oxide chiefly reacts thus:

$$SnO_2+2CHCl_3=SnCl_4+2CO+2HCl$$

(Renz, Ber. 1906, 39, 249).

When heated with hypophosphorous acid over a Bunsen flame for 30 mins., *stannous phosphate* or *pyrophosphate*, is formed; since these are readily soluble in hydrochloric acid, stannic oxide can thus be separated from silica which is not affected by this treatment (Dott, Pharm. J. 1908, 81, 585).

Stannic oxide, in the form of *putty powder*, which is a mixture of tin and lead oxides, or a stannate of lead, is used as a polishing material for glass. To avoid any possibility of danger from the use of this powder it has been recommended to mix 1 part of putty powder with 2 of metastannic acid (Gueroult, Compt. rend. 1892, 115, 757). Stannic oxide is an important factor in the manufacture of glazes and of enamels, the latter assuming an intensely white colour on the addition of a small quantity of the oxide. It is also the best material known for making opaque glaze or glass, and is employed in glaze brick and tile manufacture (Enequist, *l.c.*; Burt, Trans. Amer. Ceramic Soc. 1902, 4, 139).

Tin oxide is also said to be useful for the purification of water (J. Soc. Chem. Ind. 1894, 56).

Perstannic oxide SnO_3. W. Spring (Bull. Soc. chim. [iii.] 1, 180) has obtained a substance of the composition $H_2Sn_2O_7$, probably a hydrate of this oxide, by dialysing the turbid solution obtained by adding hydrated barium peroxide in excess to a solution of stannous chloride in hydrochloric acid, and evaporating the solution of the colloid on the water-bath.

Stannic acids. Two isomeric stannic hydroxides are known, each of which behaves as an acid and exists in various degrees of hydration between the limits H_2SnO_3 and H_4SnO_4. They are both colloidal modifications of hydrated stannic oxide, only differing in the size of their particles, the α-acid consisting of relatively small, the β-acid of relatively large particles. (Mecklenburg, Zeitsch. anorg. Chem. 1909, 64, 368; *see* also Fremy, Ann. Chim. Phys. 1844, [iii.] 12, 466; *ibid.* 1848, 23, 385; Musculus, Compt. rend. 1867, 65, 961; Vignon, *ibid.* 1889, 108, 1049; *ibid.* 109, 372; and others.)

Stannic acid, α- or ortho-stannic acid H_2SnO_3 is obtained by precipitating stannic chloride with ammonia, or by addition of calcium or barium carbonate to a solution of stannic chloride in quantity insufficient to precipitate the whole.

It is also formed by treating an alkali stannate with a mineral acid (Kühl, Pharm. Zeit. 1908, 53, 49) and by electrolysing an alkali chloride, nitrate or sulphate solution, using platinum as cathode and tin as anode (Lorenz, Zeitsch. anorg. Chem. 1896, 12, 436), and by other methods (Engel, Compt. rend. 1897, 125, 651;

Neumann, Monatsh. 12, 518; Coppadoro, Chem. Zeit. 1907, 31, Rep. 336).

Its composition varies with its mode of drying, and it is converted into anhydrous SnO_2 at 630°–655°. It forms a gelatinous substance, or white voluminous, amorphous precipitate, slightly soluble in water and of acid reaction. When dried spontaneously, it forms translucent lumps, resembling gum arabic.

When boiled with phenosafranine in the presence of sodium sulphate, stannic acid forms an intense red lake; metastannic acid under the same conditions only forms a pale rose tint (Vignon, Compt. rend. 1891, 112, 580).

A colloidal stannic acid is known (*v.* Graham, Phil. Trans. 151, 213; Van Bemmelen, Rec. trav. chim. 7, 87; Schneider, Zeitsch. anorg. Chem. 1894, 5, 83; *ibid.* 1900, 23, 111; Lottermoser, J. pr. Chem. 1899, [ii.] 59, 489; Biltz, Ber. 1902, 35, 4431). It can be prepared by the dialysis of an alkali solution of tin chloride or of a hydrochloric acid solution of potassium stannate. Colloidal stannic acid is the most important constituent of purple of Cassius (*v.* GOLD PURPLE).

Stannic acid forms a large and important series of salts, most of which are crystalline. The alkaline stannates are soluble, and may be prepared by dissolving the precipitated oxide in the alkaline hydroxide. The others are mostly insoluble, and are best obtained by double decomposition. The potassium and sodium salts are the only ones of technical importance. The stannates have been investigated by Fremy (Ann. Chim. Phys. 1844, [iii.] 12, 462; 1848, [iii.] 23, 393), Moberg (J. pr. Chem. [i.] 28, 230), Marignac (Ann. de Mines, [iii.] 15, 277), Ordway (Amer. J. Sci. [ii.] 40, 173), Ditte (Compt. rend. 1882, 94, 1114; 1883, 96, 701), and Bellucci and Parravano (Atti. R. Accad. Lincei. 1904, [v.] 13, ii. 324, 339; *ibid.* 1905, 14, i. 457).

According to the last-mentioned authors they are isomorphous with the plumbates and platinates.

Sodium stannate Na_2SnO_3 usually occurs in six-sided tables of the composition $Na_2SnO_3,3H_2O$ (Moberg, Marignac, Ordway, *l.c.*), which are less soluble in hot than in cold water. According to Ordway, 100 parts of water dissolve 67·4 parts at 0°, and 61·3 parts at 20°.

According to Bellucci and Paravanno, the water is present not merely as water of crystallisation but in a more intimate form, namely, as $Na_2Sn(OH)_6$.

Crystals of the above composition are deposited from a hot alkaline solution, but the salt may also be obtained with 8, 9, or 10 molecules of water. The form crystallising with 9 molecules is said to be obtained in oblique rhombic prisms by recrystallising the commercial salt (Jonas, Chem. Zentr. 1865, 607); while, according to Haeffely (Dingl. poly. J. 144, 66), crystals of the composition $Na_2SnO_3,3H_2O$ are deposited from hot concentrated solutions of 1·3 sp.gr., but re-dissolve on cooling to a solution of 1·35 sp.gr., from which crystals containing 8 molecules of water are gradually deposited.

Copper is readily tinned by immersion in a solution of the salt.

Sodium stannate is largely used, under the name of 'preparing salt,' as a mordant in dyeing and calico-printing, the fabric being first passed through a solution of the stannate, and then through weak sulphuric acid, which precipitates the hydrated oxide on the fibres.

For preparing this salt on the large scale, the original processes patented by J. Greenwood, J. Mercer, and J. Barnes (Eng. Pat. 10757, 1845), J. Young (Eng. Pat. 12359, 1848; 12744, 1849), and Haeffely (Eng. Pat. 603, 1854), are still used with some modifications. A number of other processes are mentioned in the list of patents relating to tin salts (*infra*).

The process of Greenwood, Mercer, and Barnes consists in heating 22 lbs. of caustic soda in an iron crucible until evolution of water ceases, and then adding 8 lbs. of sodium nitrate and 4 lbs. of sodium chloride, followed, when the mass is nearly fused, by 10 lbs. of feathered tin, with constant stirring until deflagration ensues. The mixture then becomes white hot and pasty, and is wholly converted into the stannate.

For preparing sodium '*stannite*' a mixture of 4 lbs. of sodium chloride, 1 gallon (13·5 lbs.) of caustic soda, 1 lb. of sodium nitrate, and 4 lbs. of tin is heated in an iron crucible, and the dry powder finally obtained is stirred so long as ammonia is evolved.

Young's processes—most of which are described below—consist mainly in the preparation of the stannate directly from the ore, thus avoiding the cost of obtaining and re-oxidising the metal.

By one process the native or prepared oxide is boiled in an iron pot with a quantity, varying with the tin value of the ore, of 22 p.c. soda lye, the temperature being gradually raised to about 600°F., at which combination takes place. When the operation is completed, which is ascertained by removing a portion and seeing how much dissolves, the mass is cooled in another vessel and is dissolved, filtered, or decanted, and recrystallised or sold in solution.

In another process, the ore is heated to redness with one and a half parts of sodium nitrate in a current of steam with constant stirring. The stannate is produced, with evolution of nitrous fumes and nitric acid. The nitrate may be replaced by 1 part of salt, hydrochloric acid being then obtained as the by-product.

'Stannite' of soda is obtained by heating the metal with its own weight of caustic soda, with constant stirring, or by electrolysing a concentrated solution of sodium hydroxide, using a rotating tin anode and a platinum cathode. The current must not be too strong, and the solution must be protected from oxidation by a stream of hydrogen (Goldschmidt and Eckardt, Zeitsch. physikal. Chem. 1906, 56, 385). The solution of the stannite may be used in dyeing and printing operations as it is, or it may be converted into stannate, with precipitation of tin as a black powder, by boiling.

The stannate may be obtained direct from the metal by heating a mixture of 20 parts of tin, 16 of sodium hydroxide, and 3 of manganese dioxide to redness, with constant agitation and free exposure to the air. The dioxide appears to act as a carrier of oxygen, and is obtained unchanged at the end of the operation.

In another process, calcium stannate is obtained by roasting in a reverberatory furnace a mixture of the ore with slaked lime. The product is treated with sufficient hydrochloric acid to precipitate the tin as oxide, but not to redissolve any of it, and the precipitate is dissolved in boiling soda lye. The salt may also be obtained by boiling barium stannate, obtained similarly to the lime salt, with sodium sulphate, until all the barium is converted into sulphate.

Haeffely's process consists in the preparation of a solution of 'plumbate of soda' by dissolving 54 lbs. of red lead or 70–80 lbs. of litharge in a solution of 45 lbs. of caustic soda of 70°Tw. The solution is diluted, and 16 lbs. of tin is suspended in it while boiling, so that in 4 or 5 hours the lead is obtained as a deposit, which may be readily oxidised for re-use, while sodium stannate remains in solution.

The following process has also been employed (Chem. Zeit. 9, 851):—Ten boilers, arranged in horseshoe form, and each having a central tube, the lower end of which forms a perforated funnel, are almost filled with granulated tin, and six of them are charged with soda lye of 15°Bé. The liquor is drawn off from each, after a suitable amount of boiling, through a siphon passed into the central tube, and is passed from boiler to boiler until of 30°Bé., when it is allowed to settle in a tank. For preparing 'sodium stannate liquor,' enough common salt is dissolved in the solution to reduce the proportion of tin to 5 p.c.; and for producing the solid the liquid is evaporated and calcined, and mixed with enough sodium chloride to reduce the tin to 42 p.c.

A *sodium arsenio-stannate*

$$Na_2O{\cdot}6SnO_2{\cdot}2As_2O_5,5H_2O,$$

occurring in shining needles, is sometimes used instead of the ordinary stannate, and is said to give brighter colours and to be more economical. It is prepared by adding nitric acid to a boiling solution of sodium stannate and sodium arsenate, and treating the resulting precipitate of $2SnO_2{\cdot}As_2O_5,10H_2O$ with excess of soda (*v.* Haeffely, Dingl. poly. J. 140, 290; J. Mercer and W. Blythe, Eng. Pat. 12807, 1849). In the latter process a sodium phosphostannate is also employed for the same purposes. Another sodium arsenio-stannate

$$Na_2SnO_3 5Na_3AsO_4,60H_2O$$

has been obtained by Prandtl (Ber. 1907, 40 2133).

Potassium stannate K_2SnO_3 is obtained similarly to the sodium salt, and is sometimes employed in dyeing and calico-printing. It crystallises from spontaneously evaporated solutions in transparent oblique rhombic prisms of the composition $K_2SnO_3,3H_2O$ (Marignac, Ann. de Mines, [v.] 15, 277; Moberg, J. pr. Chem. [i.] 28, 230; Ordway, Amer. J. Sci. [ii.] 40, 173). It becomes anhydrous when heated to redness.

Potassium stannate is insoluble in alcohol, but dissolves in water to an alkaline solution, 100 parts of water dissolving 106·6 parts at 10° and 110·5 parts at 20° (Ordway, *l.c.*).

Cupric stannate $CuSnO_3$ has been employed as a green pigment. It is prepared for this purpose by precipitating sodium stannate with copper sulphate, or by addition of a solution of 118 parts of tin in *aqua regia* to a solution of 250 parts of copper sulphate, with subsequent addition of sodium hydroxide in excess.

Chromium - tin compounds. A so-called chromium stannate or 'pink colour,' used for producing a blood-red colour in pottery glaze, is prepared by heating a mixture of 10 parts of stannic oxide, 34 parts of calcium carbonate, 5 parts of silica, 1 part of alumina, and 3–4 parts of crystallised potassium chromate for several hours in a closed crucible. The red compound produced gives a fine rose-coloured product when washed with dilute hydrochloric acid.

A substance known as *mineral lake*, possessing a fine lilac colour, is used in colouring paper hangings and for oil painting. It consists of a mixture of chromium oxide and excess of stannic oxide, and can be prepared by igniting together 1 part of the former with 50 of the latter (Leykauf, J. pr. Chem. 1892, 19, 127), or by dissolving potassium chromate in 5 or 6 parts of water, and adding this solution to a solution of stannous chloride until precipitation ceases. The damp, washed precipitate is ground with half its volume of nitre, and dried, and the finely-powdered mixture is thrown in small portions into a crucible heated to redness and containing some potassium nitrate. After pouring off the supernatant fused salt, the pale-yellow residue is washed free from alkali, and is calcined at a strong heat in a luted crucible until it becomes dense and acquires the desired colour.

A series of 'pinks' have been prepared by moistening equal portions of calcium stannate or mixtures of tin dioxide and whiting with varying proportions of a solution of ammonium dichromate. The mixtures are then dried, fired, cooled, and washed with hot water. The products all contain a more or less constant quantity of chromium, and it is probable that they consist of the colouring agent, chromium oxide, resting on a base of stannic oxide (Lethbridge, Trans. Engl. Ceramic Soc. 1903–1904, **9**: *see* also Hull, Trans. Amer. Ceramic Soc. 1902, **4**, 230).

Stannates of many other metals and thiostannates have also been obtained.

Metastannic acid or **β-stannic acid** is obtained as a white insoluble powder, with evolution of nitrous fumes, when tin is treated with strong nitric acid (Engel, Compt. rend. 1897, **124**, 765; *ibid.* 125, 709; Van Leent, Rec. trav. chim. 1898, 17, 86).

It is also obtained by the ready isomerisation of stannic acid, as when a hydrochloric or hydrobromic acid solution of the latter is allowed to stand (Lorenz, Zeitsch. anorg. Chem. 1895, 9, 376).

Its degree of hydration, like that of stannic acid, depends on the process used for drying (*see* Frémy, Weber, &c.).

Metastannic acid is insoluble in nitric acid (*cf.* Jörgensen, Zeitsch. anorg. Chem. 1908, **57**, 353). It swells up in concentrated sulphuric acid, the product being soluble in water and alcohol, but decomposing into the two acids on boiling. Hydrochloric acid converts it into a chloride of metastannic acid, which is soluble in water but not in hydrochloric acid, and which is reprecipitated from solution in the gelatinous form on boiling, or on addition of much hydrochloric acid.

It is insoluble in ammonia, except when

freshly-precipitated from a cold solution of a metastannate by an acid, but dissolves in alkaline hydroxides and carbonates, with formation of mestastannates.

A colloidal metastannic acid is known (*v.* Graham, Phil. Trans. 151, 213; Van Bemmelen, Rec. trav. chim, 7, 87; Liebschutz, Chem. News, 1910, 102, 213).

The meta- acid is said to have a tendering effect on silk fibres (Heermann, Färber Zeit. 1908, 19, 318; Bayerlein, *ibid.* 1908, 18, 241).

The salts of metastannic acid appear to indicate that the acid has the formula

$$5(SnO_2 \cdot H_2O), \textit{ i.e. } H_2Sn_5O_{11},4H_2O,$$

but it is generally considered to have the same composition as stannic acid.

The metastannates are difficultly crystallisable. When strongly heated, they decompose into stannic oxide and the base. *Potassium metastannate* $K_2Sn_5O_{11},4H_2O$ is a strongly alkaline salt obtained by dissolving the acid in potash. It is precipitated from aqueous solution by a neutral alkaline salt or by ammonium chloride. *Sodium metastannate* $Na_2Sn_5O_{11},4H_2O$ is a slightly soluble granular salt obtained like the potassium salt. A hard gummy precipitate of the composition $Na_2Sn_9O_{19},8H_2O$ is obtained by addition of caustic soda to a solution of the above compound of hydrochloric acid and metastannic acid.

Thiometastannates are also known.

Perstannic acid $HSnO_4,2H_2O$ is formed when stannic acid is treated with excess of 30 p.c. hydrogen peroxide and the mixture heated to about 70°. On heating to 100° it yields the acid $H_2Sn_2O_7,3H_2O$. The alkali stannates when similarly treated form the salts corresponding to these acids (Tanatar, Ber. 1905, 38, 1184). When concentrated alkali stannates are electrolysed at low temperature with a low current density they also form perstannates (Coppadoro, Gazz. chim. ital. 1908, 38, i. 489, and *l.c.*).

Salts of tin with oxyacids. These salts, although numerous, are of little technical importance, but a number of solutions containing them are used in dyeing and calico-printing. *Stannous sulphate* $SnSO_4$ is obtained as a crystalline powder by evaporating *in vacuô* a solution of tin or stannous hydroxide in dilute sulphuric acid. *Stannic sulphate* $Sn(SO_4)_2$ is obtained as a white salt, soluble in dilute sulphuric acid but mostly precipitated on dilution, by dissolving the hydroxide in sulphuric acid. According to Ditte (Compt. rend. 1887, 104, 172), a solution of stannic hydroxide in warm dilute sulphuric acid (1–8) deposits, on concentration, first radiating needles, then rhomboidal lamellæ, and finally hexagonal prisms, all colourless and all possessing the composition $Sn(SO_4)_2,2H_2O$. He has obtained the same product by the action of sulphuric acid on metastannic acid. The crystals deliquesce to a clear liquid. The solution is decomposed, on dilution, with precipitation of the hydroxide. A number of double tin sulphates are known (Weinland and Kühl, Ber. 1906, 39, 2951; Zeitsch. anorg. Chem. 1907, 54, 244). *Stannous nitrate* $Sn(NO_3)_2$ is obtained by dissolving tin or stannous hydroxide in very dilute nitric acid (R. Weber, J. pr. Chem. [ii.] 26, 121; Walker, Chem. Soc. Proc. 1893, 114; Engel, *l.c.*).

A basic salt of the composition $2SnO \cdot N_2O_5$ is obtained as a white crystalline precipitate by adding a solution of sodium carbonate to the neutral salt in quantity insufficient for complete precipitation. It may also be obtained by digesting the normal salt with stannous hydroxide. It deflagrates at 100°, or on friction. *Stannic nitrate* $Sn(NO_3)_4$ crystallises in silky tablets from a solution of stannic hydroxide in nitric acid.

It is also formed by dissolving tin in 70 p.c. nitric acid (Montemartini, Gazz. chim. ital. 1892, 22, 384).

The so-called 'nitrate of tin' or 'physic' used by dyers is a mixture of stannous and stannic chlorides (*v. Stannous chloride, infra*). A solution of tin in nitric acid is, however, also used in dyeing (*v.* Crookes, Handb. of Dyeing and Calico Printing, 1874, 527).

Stannous sulphide SnS is obtained as a tough, crystalline, bluish-grey fusible mass by heating tin with sulphur, or in crystalline scales by fusing the sulphide so obtained with stannous chloride and treating the product with dilute hydrochloric acid. The crystalline sulphide may also be obtained by heating the amorphous form in the electric furnace (Mourlot, Compt. rend. 1897, 124, 768). It is obtained as a brown powder, which blackens on drying, by precipitating stannous chloride with sulphuretted hydrogen.

Stannous sulphide is insoluble in normal ammonium sulphide, but dissolves in the yellow sulphide and in alkaline polysulphides (*v.* Ditte, Compt. rend. 1882, 94, 1419), and, with evolution of sulphuretted hydrogen and formation of stannous chloride, in hot hydrochloric acid. Hydrogen chloride acts similarly on the warmed, but not on the cold, sulphide (Ditte, *ibid.* 1883, 97, 42).

Stannous sulphide is sometimes soluble, at other times insoluble, in sodium hydroxide, the cause of this variation being unknown (Perkin, J. Soc. Chem. Ind. 1901, 425).

Pure stannous sulphide has m.p. 880° (Pélabon, Compt. rend. 1906, 142, 1147). It is slightly radioactive (Campbell, Proc. Cambridge Philos. Soc. 1906, 13, 282).

Stannic sulphide SnS_2 cannot be prepared by simply heating tin and sulphur together, because the heat generated is sufficient to reduce the disulphide to monosulphide, but it may be so obtained when sufficient ammonium chloride or other volatile substance is present to moderate the action. Woulfe (Phil. Trans. 1771, 61, 114; also Gmelin's Handbook, 5, 79) describes a number of methods of preparing this compound, which is used as a bronze powder for bronzing articles of gypsum, wood, &c.

Various mixtures of tin chloride and sulphur, or tin, sulphur, and ammonium chloride, or tin amalgam or tin sulphide with sulphur and ammonium chloride, are heated in retorts or covered crucibles, at first gently for a few hours, then more strongly, but not quite to redness. On cooling the greater portion of the sulphide is at the bottom, but the purer and finer crystals are found sublimed at the top.

Crystalline stannic sulphide, sp.gr. 4·425, is often known as 'Mosaic gold,' *aurum mosaicum*, or *musivum.* For a reddish shade, 50 grms. of 50 p.c. tin amalgam, 25 of crystallised stannous chloride, 35 of ammonium chloride, and 35 of sulphur are finely powdered together and ignited gradually in a glass retort covered with asbestos, in the flame of a large blow-pipe, which is moved about periodically. During the operation the colour of the mass should be dark brown. If it becomes black owing to the formation of stannous sulphide, the flame should be lowered. For yellowish shades, 50 grms. of crystallised stannous chloride and 25 grms. of flowers of sulphur are employed. The yield is 57 p.c. of the theoretical (Langutt, Zeitsch. angew. Chem. 1897, 557). *V.* GOLD, MOSAIC.

When heated, stannic sulphide sublimes, with partial decomposition into sulphur and stannous sulphide. It dissolves readily in alkalis, but not in acids, except *aqua regia.* It fuses in a current of chlorine, and absorbs 6 molecules of the gas, forming a yellow crystalline compound of the composition $SnCl_4,2SCl_4$ (Rose, Pogg. Ann. 42, 517). When heated with iodine in a current of carbon dioxide it gives a brown, crystalline, fusible mass of the composition SnS_2I_4 (Schneider, J. pr. Chem. [i.] 79, 419).

The dirty-yellow precipitate obtained by passage of sulphuretted hydrogen through a solution of a stannic salt consists of a mixture of stannic sulphide and stannic hydroxide; this dissolves in alkaline sulphides, with formation of thiostannates (Kühn, Annalen, 1852, 84, 110), and also in alkalis and hydrochloric acid. Ditte (Compt. rend 1882, 95, 641) describes several double sulphides or thiostannates and also seleniothio-stannates.

Hydrogen chloride or bromide convert the sulphide into the corresponding halide (Kelley and Smith, Amer. Chem. J. 1896, 18, 1096).

When stannic sulphide is allowed to remain in contact with ammonia, filtered, and the filtrate acidified, a white mass of an amorphous stannic sulphide is formed. It dissolves readily in ammonia to an orange-red solution, and becomes yellow on drying (Schmidt, Ber. 1894, 27, 2739; Chem. Zentr. 1907, i. 397; Materne, *ibid.* 1906, ii. 557; Lang and Carson, J. Soc. Chem. Ind. 1902, 1018). When dried in air it loses a little sulphur and becomes dark brown, hard, and brittle. This sulphide behaves like a colloidal sulphide. Colloidal stannic sulphide has been obtained (Spring, Ber. 1883, 16, 1142; Schneider, Zeitsch. anorg. Chem. 1894, 5, 83; *see* also Biltz, Chem. Zentr. 1904, i. 1040).

Tin sesquisulphide Sn_2S_3 is obtained by gentle ignition of 3 parts of stannous sulphide and 1 of sulphur in a retort. It forms a yellowish-grey mass of metallic lustre (Antony and Niccoli, Gazz. chim. ital. 1892, 22, ii. 408).

Stannous selenide SnSe is obtained with incandescence when selenium is heated with tin, as a light-grey lustrous body of crystalline fracture, not reducible by hydrogen. It is obtained as a dark-brown precipitate, which becomes nearly black on drying, by passing seleniuretted hydrogen into stannous chloride solution. It dissolves in alkalis and akaline sulphides (*v.* Uelsmann, Annalen, 1860, 116, 124; Pélabon, *l.c.*).

Stannic selenide $SnSe_2$ is obtained by passing seleniuretted hydrogen into stannic chloride solution as a yellowish-red precipitate which dries to a brown powder, soluble in caustic alkalis and alkaline sulphides, and forming stannous selenide when heated in hydrogen.

According to Little (Annalen, 1859, 112, 213), is obtained as a tin-white, lustrous, easily-fusible mass, unaffected by hydrochloric acid, but readily decomposed by nitric acid, by heating tin in selenium vapour. Ditte (Compt. rend. 1882, 95, 641; *ibid.* 1887, 104, 174) describes some double selenides corresponding with the thiostannates (*v. Stannic sulphide*).

A telluride is also known.

Stannous chloride $SnCl_2$ is obtained in the anhydrous condition by heating tin in hydrogen chloride, or by heating a mixture of equal weights of 'feathered' (*i.e.* granulated) tin or filings and mercuric chloride; and in monoclinic prisms of the composition $SnCl_2,2H_2O$ (O. Henry, J. Pharm. 12, 134) by evaporating a solution of tin in hydrochloric acid.

Stannous or stannic chloride may be obtained as desired by the following process: Stannous chloride, formed by the action of a solution containing chlorine on tin, is subjected to the action of a gaseous or fluid mixture containing free chlorine, hydrochloric acid, and air or oxygen (Young, J. Amer. Chem. Soc. 1901, 23, 119, 450). Stannic chloride is thus formed which when made to react with tin reforms stannous chloride (U.S. Pats. 810454, 810455, 810456, 810897, 1906; D. R. P. 184494). For other methods, *see* D. R. PP. 176456, 176457, 181876, 188018).

The crystals melt at 40°, and at 100° lose most of their water, together with a little hydrochloric acid. When dried *in vacuô*, or over sulphuric acid, they become anhydrous.

The anhydrous chloride fuses at 249·3° to an oil which boils at 617°–628° (Carnelley and Carleton Williams, Chem. Soc. Trans. 1879, 563). or, according to Biltz and V. Meyer (Ber. 1888, 21, 22), at 606·1°. The anhydrous chloride is sometimes called 'butter of tin,' although that term is usually applied to the hydrated tetrachloride. Stannous chloride is soluble in water and alcohol. On dilution, the aqueous solution becomes turbid, from precipitation, with separation of hydrochloric acid, of a basic chloride $2SnO,HCl,H_2O$, which is also formed when the clear solution is exposed to the air. Mallet (Chem. Soc. Trans. 1879, 524) has observed a gelatinous deposit of the composition $SnO_2{\cdot}HCl$, to which he has applied the term *chlor-stannic acid*, in a solution of stannous chloride after long standing. Donath (Rep. Anal. Chem. 7, 77) considers that this compound is produced, together with stannic hydroxide, by the action of light on aqueous stannous chloride.

R. Engel (Compt. rend. 1888, 106, 1398) has obtained a compound of the composition

$$SnCl_2,HCl,3H_2O,$$

which he calls *chlorostannic acid*, by passing chlorine over the hydrate $SnCl_2,2H_2O$. The crystals fuse to a clear liquid having the above composition, and depositing, when cooled to −40°, slender silky needles which melt at about −27°. According to Ditte (*ibid.* 1883, 97, 42), however, the liquid contains a chloride of the composition $SnCl_2,H_2O$, which is also formed by the action of concentrated hydrochloric acid on the chloride $SnCl_2,2H_2O$.

When stannous chloride is electrolysed crystalline tin can be obtained (Saposhnikoff, J. Russ. Phys. Chem. Soc. 1905, 37, 153).

Stannous chloride forms crystalline double chlorides with the alkalis (*v.* Benas, Chem. Zentr. 1884, 957, forming salts of the composition $SnCl_2{\cdot}KCl,H_2O$ and $SnCl_2{\cdot}2KCl,H_2O$). It absorbs dry ammonia, with formation of a compound of the composition $SnCl_2{\cdot}NH_3$, and also $SnCl_2{\cdot}2NH_3$ (Naumann, Ber. 1910, 43, 313).

Stannous chloride is soluble in alcohol and in ether, the latter solution gives a brownish-red ring when added to hydrochloric acid containing 1/50 mgrm. of arsenious acid (Jong, Zeitsch. anorg. Chem. 1902, 41, 596).

Like other stannous salts, stannous chloride is a strong reducing agent and is employed as such, both for the reduction of organic and inorganic compounds. It is also used in the analysis of a number of substances (Henriet, Compt. rend. 1901, 132, 966; Weil, *ibid.* 1902, 134, 115).

A small quantity of stannous chloride is said to increase the yield of alcohol in fermentation processes; it also accelerates the revivification of the yeast sown in must, and cultures taken from the yeast so formed retain a similar property for a certain length of time (Gimel, Compt. rend. 1908, 147, 1324).

Stannous chloride and other stannous salts are largely used in dyeing and calico-printing under the name 'tin salts' or 'tin crystals' (Dreher, Färber-Zeit. 7, 145; Reisz, *ibid.* 221, 222; Binder, Bull. Soc. Ind. Mulhouse, 1900, 92; Paterson, J. Soc. Dyers Col. 1906, 22, 188; Coberti, J. Soc. Chem. Ind. 1899, 829).

Stannic chloride $SnCl_4$ was first prepared by Libavius in 1605, who obtained it by distilling a mixture of tin or its amalgam with excess of mercuric chloride; he termed the product *Spiritus argenti vivi sublimati.* It may also be prepared by the action of chlorine (Lorenz, Zeitsch. anorg. Chem. 1895, 10, 44; Beckmann and Geib, *ibid.* 1906, 51, 96); or phosphorus pentachloride on tin (Goldschmidt, Chem. Zentr. 1881, 489); or by the action of chloroform on stannic oxide (Renz, Ber. 1906, 39, 249). Technically, it is generally prepared by the action of chlorine or hydrochloric acid on tin-plate waste or tin waste residues from dye works and a large number of patents have been registered for this purpose (*see* Fr. Pats. 371067, 1906; 392615, 401125, 405851, 406300, 1909; Heermann, Färber Zeit. 1907, 18, 34; U. S. Pats. 884756, 877261, 877248, 1908; 976990, 958986, 1910; D. R. P. 222838; J. Soc. Chem. Ind. 1907, 253; *ibid.* 1908, 160; *ibid.* 1909, 21, 1087; *ibid.* 1910, 424, 1105; *see* also U. S. Pats. 883140, 883141, 1908; Fr. Pats. 386594, 388089, 1908).

The chloride distils over as a colourless mobile liquid, boiling at 113·89° at 760 mm. pressure (Thorpe, Chem. Soc. Trans. 1880, 37, 331), and solidifying at —33° to small white crystals (Besson, Compt. rend. 1889, 109, 940).

The liquid has sp.gr. 2·2788 at 0°/4° (Thorpe, *loc. cit.*), and, owing to its high refractive index, presents a very brilliant appearance.

When exposed to the air, it emits dense white fumes, and is finally converted into a crystalline hydrate $SnCl_4.5H_2O$ (Lewy, Compt. rend. 1845, 21, 369), which is also obtained, with evolution of heat, by mixing stannic chloride with one-third its weight of water. This hydrate is sometimes known as 'butter of tin,' or, by the dyers, as 'oxymuriate of tin.' Hydrates of the composition $SnCl_4.3H_2O$ and $SnCl_4.8H_2O$ are also known. For the sp.gr. of various solutions of this salt, *see* Heerman (Chem. Zeit. 1907, 31, 680).

On hydrolysis, it first forms the intermediate compound $SnCl_3OH$, and then stannic acid; by alcoholysis it gives the compound $SnCl_3OEt$ (Pfeiffer, Ber. 1905, 38, 2466; von Biron, J. Russ. Phys. Chem. Soc. 1906, 37, 963).

Stannic chloride forms crystalline double chlorides, sometimes called *chloro-stannates* or *stannichlorides* with the alkaline chlorides (Bellucci and Parravano, Atti. R. Accad. Lincei. 1904, v. 13, ii. 307; von Biron, J. Russ. Phys. Chem. Soc. 1904, 36, 489, 933; *ibid.* 1905, 37, 963, 994, 1036; Weinland and Bames, Zeitsch. anorg. Chem. 1909, 62, 250); thus, $SnCl_4{\cdot}2KCl$ and $SnCl_4{\cdot}2NH_4Cl$, the latter forming the 'pink salt' formerly much used by dyers.

Stannic chloride dissolves phosphorus and iodine, and mixes with bromine and carbon disulphide. It converts mercury into calomel, and is itself decomposed by nitric acid, with precipitation of metastannic acid. Among the substances produced by direct combination with other compounds may be mentioned $SnCl_4{\cdot}2NH_3$, a soluble volatile solid (Rose, Pogg. Ann. 16, 63); $3SnCl_4{\cdot}2PH_3$, a yellow fuming solid (Rose, *ibid.* 24, 159); $SnCl_4{\cdot}N_2O_3$, a yellow amorphous mass; $SnCl_4{\cdot}SO_3$ a white solid (Rose, *ibid.* 44, 320); $SnCl_4{\cdot}PCl_5$ and $SnCl_4{\cdot}POCl_3$ (Casselmann, Annalen, 1852, 83, 257); $SnCl_4 2(C_2H_5)_2O$, a white crystalline compound (Coldridge, Phil. Mag. [v.] 29, 383, 480). A yellow crystalline substance $SnCl_4{\cdot}2SCl_4$, fusing below 30°, is obtained by the action of chlorine on stannic sulphide (Rose, Pogg. Ann. 42, 517).

When a cooled solution of stannic chloride in chloroform is treated with nitric peroxide, the compound $3SnCl_4{\cdot}4NOCl$ is formed (Thomas, Compt. rend. 1896, 122, 32), whilst if such a solution is treated with nitrogen sulphide dissolved in chloroform, red crystals of the substance $SnCl_4{\cdot}2N_4S_4$ are deposited (Davis, Chem. Soc. Trans. 1906, 1576).

Stannic chloride absorbs large quantities of chlorine at low temperatures, with considerable increase in volume and lowering of the melting-point (Besson, Compt. rend. 1889, 109, 940).

Stannic chloride is used in dyeing as a mordant, and silk is weighted with it before dyeing (Froenkel and Fasal, J. Soc. Chem. Ind. 1898, 148; *ibid.* 1904, 899). Its use for this purpose is said to have been discovered by the Dutch chemist, Drebbel, in 1630, who found that cochineal gives a permanent brilliant red dye in the presence of dilute stannic chloride.

A patent was taken out in England as early as 1748 by O. Pawl (Specification No. 630, 1748) for the use of tin dissolved in *aquafortis*, with addition of ammonium chloride, for dyeing scarlet.

The older methods of preparing tin salts for this purpose, whereby tin is dissolved in excess of hydrochloric acid, and the solution is oxidised by means of chlorates, have the disadvantage of producing a very impure product. The mordanting and weighting is due only to the stannic chloride and the impurities tend to weaken the fibres, to make the latter more sensitive to light, and to bring about the gradual deterioration in the strength of the material. To avoid this, Sperry has devised a special apparatus whereby pure anhydrous stannic chloride may be prepared by the treatment of impure tin bearing materials with ordinary commercial chlorine (J. Soc. Chem. Ind. 1908, 312, 404, 628, 749, 978; Eng. Pat. 389188; U. S. Pats. 882354, 887538, 885391. For Fig. and description of apparatus, *see* J. Soc. Chem. Ind. 1908, 313). From the pure stannic chloride thus prepared all the compounds of tin needed by dyers may be obtained in pure condition.

A solution consisting of stannic and stannous chloride, obtained by dissolving tin in *aqua regia*, is used in the preparation of fuchsine under the name 'nitrate of tin' or 'physic' (*see* above).

It is now more usual, however, to employ the crystalline pentahydrate $SnCl_4,5H_2O$.

A solution consisting of stannic chloride, containing more or less stannous chloride, and used in dyeing under the name 'oxychloride of tin' or 'pink cutting liquid,' is prepared by adding 1 part of stannous chloride to 1½ parts of nitric acid of sp.gr. 1·31 in portions, with constant stirring, to prevent boiling over from the violence of the action; or by dissolving 337 parts of stannous chloride in 300 parts of hydrochloric acid (20°Tw.), with the aid of a minimum of water, and adding gradually 58 parts of potassium chlorate.

In small quantities stannic chloride may be added to the sizing mass for cotton warps in order to prevent the too rapid decomposition of the size (Textile Colorist, 1893, 15, 7).

For the detection of tin in mordanted cloth, *see* Paterson (J. Soc. Dyers Col. 1906, 22, 189); Silbermann (Bull. Soc. chim. Mulhouse, 1906, 76, 357).

A rapid and delicate method for detecting sodium chloride in commercial stannic chloride, consists in precipitating the former with 99·5 p.c. alcohol saturated with hydrogen chloride (Heermann, Chem. Zeit. 1907, 31, 27).

Stannous bromide $SnBr_2$ is obtained in solution by dissolving tin in hydrobromic acid (Balard, Ann. Chim. Phys. 1826, [ii.] 32, 337). It may be obtained as an anhydrous, pale-yellow, crystalline mass by heating tin in hydrobromic acid vapour and re-distilling the product (Freyer and Meyer, Zeitsch. anorg. Chem. 1892, 2, 1).

According to Rayman and Preis (Annalen, 1884, 223, 323), it melts at 215·5° to a pale-yellow oily liquid, of sp.gr. 5·117 at 17°. According to Carnelley and Carleton Williams (Chem. Soc. Trans. 1879, 564), it melts at 259°, and boils at 617°–634°.

A hydrate $SnBr_2,H_2O$ separates in needles or thin plates from the greenish solution of tin in warm concentrated hydrobromic acid. It loses its water in dry air, or when heated to 70°–80°. It dissolves in a little water, but is decomposed by excess, with precipitation of a gelatinous precipitate (*v.* Benas, Chem. Zentr. 1884, 957). A hydrate $SnBr_2,2H_2O$, crystallising in large monoclinic tables, is also obtained from the solution of tin in hydrobromic acid (Benas, *l.c.*).

Benas, Rayman and Preis have also described compounds of stannous bromide with potassium and ammonium bromides.

Stannic bromide $SnBr_4$ was discovered in 1826 by Balard (Ann. Chim. Phys. [ii.] 32, 337). It is obtained by adding bromine drop by drop to strips of tin, the temperature being kept between 35° and 59° (Lorenz, Zeitsch. anorg. Chem. 1895, 9, 366); or preferably, on account of the violence of the action with pure bromine, by gradually adding the tin to a solution of bromine in carbon disulphide, or by passing the vapour of bromine over heated tin (Carnelley and O'Shea, Chem. Soc. Trans. 1878, 55).

Stannic bromide forms a white iridescent deliquescent mass, which, by distillation, is obtained in small, well-formed, highly lustrous crystals, melting at 30° and boiling at 210° (uncorr.) (Carnelley and O'Shea, *l.c.*), or at 203° (corr.) (Rayman and Preis, Chem. Zentr. 1882, 773), and having a sp.gr. of 3·349 at 3·5° (Rayman and Preis, *l.c.*).

It fumes in the air, and dissolves readily in water. The solution deposits stannic hydroxide on heating or after standing. A hydrate $SnBr_4,4H_2O$ is obtained in colourless transparent, fuming crystals, by exposing the anhydrous bromide to moist air, or by dissolving in a little water and evaporating over sulphuric acid. Oxybromides $Sn_2Br_6O,12H_2O$ and $SnBr_8O_2,10H_2O$, obtained from stannic bromide, and a compound $SnBr_4{\cdot}2NH_3$, obtained by absorption of ammonia by the warmed bromide, are also known (Rayman and Preis, *l.c.*).

Stannic bromide unites with ether to form a deliquescent crystalline body $SnBr_4(C_2H_5)_2O$ (Niklès, Compt. rend. 1861, 52, 869). By evaporating solutions of the mixed bromides, Raymond and Preis (*l.c.*) have obtained the following double bromides or stannibromides: $2NaBr{\cdot}SnBr_4,6H_2O$, in pale-yellow, soluble crystals; $CaBr_2{\cdot}SnBr_4,6H_2O$, in slender deliquescent needles; $MgBr_2{\cdot}SnBr_4,10H_2O$, in pale-yellow, deliquescent tables; $MnBr_2{\cdot}SnBr_4,6H_2O$, in large, pale-yellow, deliquescent crystals; $FeBr_2{\cdot}SnBr_4,6H_2O$, in greenish, granular crystals; $NiBr_2{\cdot}SnBr_4,8H_2O$, in apple-green, granular, deliquescent crystals; and

$$CoBr_2{\cdot}SnBr_4,10H_2O,$$

in yellowish-red, deliquescent tablets (*see also* Leteur, Compt. rend. 1891, 113, 540).

Stannous iodide SnI_2 is obtained by dissolving tin in concentrated hydriodic acid. At the ordinary pressure solution is extremely slow, but it proceeds more rapidly in a sealed tube at 120°–150° (Wöhler and Dünhaupt, Annalen, 1853, 86, 374). It may also be obtained in yellowish-red needles, slightly soluble in water, and readily soluble in solutions of alkaline chlorides and iodides, and in hydrochloric acid, by addition of potassium iodide in slight excess to a concentrated solution of stannous chloride (Warden, Pharm. J. 1897, 58, 61). The aqueous solution is decomposed by much water, with separation of hydriodic acid and a yellow, insoluble body the composition of which varies with the amount of water present (Personne, Compt. rend. 1862, 54, 216).

Stannous iodide melts at 316° (Carnelley and Carleton Williams, Chem. Soc. Trans. 1879, 564) and volatilises at a red heat. It absorbs dry ammonia, with formation of a white body having the composition $2NH_3{\cdot}SnI_2$ (Rammelsberg, Pogg. Ann. 48, 169; Ephraim and Schmidt, Ber. 1909, 42, 3856). It unites with other metallic iodides, with hydrogen iodide (Young, J. Amer. Chem. Soc. 1897, 19, 851), and with stannous chloride.

Stannic iodide SnI_4 is obtained in yellowish-red octahedra by heating tin filings, preferably moistened with carbon disulphide, with iodine to a temperature above 50°.

It has sp.gr. 4·696 at 11° (Bödeker, Die

Beziehung zwischen Dichte und Zusammensetung, &c., Leipzig, 1860), m.p. 146° and b.p. 295° (Personne, J. 1862, 172), m.p. 143°, b.p. 341° corr.) (Emich. Monatsh. 1904, 25, 907). It sublimes at 180°.

It dissolves in carbon disulphide, ether, alcohol, chloroform, and benzene. Water decomposes it into stannic hydroxide and hydriodic acid.

By the action of ammonia on stannic iodide, dissolved in carbon disulphide, a white substance $SnI_4.8NH_3$, insoluble in water, is formed (Ephraim and Schmidt, *l.c.*).

Stannous fluoride SnF_2 is obtained in small, opaque, white, monoclinic tables of sweetish astringent taste, by evaporating a solution of stannous hydroxide in hydrofluoric acid.

Stannic fluoride SnF_4 is obtained in aqueous olution by dissolving the hydrated dioxide in hydrofluoric acid; or as a hygroscopic, white crystalline substance by the action of anhydrous hydrofluoric acid on stannic chloride (Ruff and Plato, Ber. 1904, 37, 673). It has sp.gr. 4·78 at 19°, b.p. 705°, but sublimes below this emperature. It combines with other fluorides orming a characteristic series of crystalline double salts, the *stannifluorides*, which are isomorphous with the corresponding fluorides of titanium, germanium, zirconium, and silicon Marignac, J. 1859, 110; Emich, Monatsh. 1904, 25, 907; Ruff and Albert, Ber. 1905, 38, 55; Hall and Smith, Chem. Zentr. 1905, ii. 1162).

A number of mixed halogen compounds, such as $SnCl_3Br$, $SnCl_2I_2$, $SnBr_3I$, &c., have been described (Besson, Compt. rend. 1897, 124, 383; Lenormand, J. Pharm. Chim. 1898, [vi.] 8, 249; *ibid.* 1899, 10, 114). According to Auger (Compt. rend. 1909, 149, 860), most of these compounds are only mixtures, thus, $2SnBr_2I_2=SnBr_4+SnI_4$, &c.

Phosphides. Tin combines directly with phosphorus, forming a series of phosphides, which are used for the production of phosphor-bronze (Emmerling, Ber. 1879, 12, 155; Natanson and Vortmann, *ibid.* 1877, 10, 1460; Künzel, Dingl. poly. J. 1888, 270, 166; D. R. P. 103966; Stead, J. Soc. Chem. Ind. 1897, 206).

Tin phosphide Sn_4P_3 has a silver-white colour, crystallises in spangles, sp.gr. 5·18, and begins to dissociate at 480°.

The phosphide SnP is also a crystalline substance, sp.gr. 4·10. It has a metallic appearance, begins to dissociate into phosphorus and Sn_4P_3 at 415°, and is attacked violently by fuming nitric acid (Jolibois, Compt. Rend. 1909, 48, 636). Other phosphides have also been decribed.

An unstable *tin carbonate* Sn_2CO_3 is also known (Deville, Ann. Chim. Phys. 1852, [iii.] 35, 4, 48; *see* also Moissan, Compt. rend. 1897, 125, 840).

Organic Compounds of Tin.

Stannous acetate, *oxalate*, *citrate*, and *tartrate* are employed in dyeing and calico-printing, being generally prepared by addition of an alkaline salt of the acid to a solution of stannous chloride, or by dissolving the precipitated hydroxide in the acid. Liechti and Schwitzer (Mittheilungen des Tech. Gew. Museums, 1886, 41) have indicated the value of some of these as mordants (Platsch, Zeitsch. anorg. Chem. 1899, 20, 308; Rosenheim and Aron, *ibid.* 1904, 39, 171; Paterson, *l.c.*; Henderson, Orr, and Whitehead, Chem. Soc. Trans. 1899, 555).

The ancient Egyptians are believed to have used basic tin citrates (prepared by the action of lemon juice or citric acid on tin), as a mordant, in dyeing the tapestries discovered in the tombs of Antinoa (Gilliéron, Bull. Soc. Mulhouse, 1907, 77, 148). Basic tin citrate forms a very efficient mordant for yellow dyes on wool, giving pure intense colours.

Stannous formate is prepared by dissolving precipitated stannous hydroxide in dilute formic acid. It forms white anhydrous crystals, which decompose above 100° (Goldschmidt, Chem. Zeit. 1907, 31, 608).

Tin forms a number of alkyl derivatives of the type SnR_4, $SnR^1R^2R_2{}^3$, &c. (Letts and Collie, Chem. Soc. Proc. 1886, 166; Pope and Peachy, *ibid.* 1903, 290; Polis, Ber. 1889, 22, 2915; Pfeiffer and Schnurmann, *ibid.* 1904, 37, 319; Werner, Zeitsch. anorg. Chem. 1898, 17, 99; Pfeiffer, *ibid.* 1910, 68, 102).

Methyl stannonic acid or **methyl stannoxylic acid** $MeSnO{\cdot}OH$ is formed when a mixture of methyl iodide, stannous chloride, and potassium hydroxide is allowed to stand for a day or two and the alkali is then removed by passing carbon dioxide into it. It can also be obtained pure by treating methyl stannic bromide or iodide with ammonia. It is an odourless white powder, insoluble in water and organic solvents, but soluble in mineral and some organic acids, and in alkali hydroxides. With hydrobromic acid it yields *methyl stannic bromide* or methyl stannibromoform $SnMeBr_3$, m.p. 53°, which has also been obtained by other methods. The corresponding *iodide* or iodoform, $MeSnI_3$, m.p. 86°, and the compounds $SnMe_2Br_2$; $SnMe_2O$; $SnMeS{\cdot}SH$ and methyl stannichloroform, m.p. 105°–107°, b.p. 179°–180°, have also been prepared (Pfeiffer and Lenhardt, Ber. 1903, 36, 1054, 3027; Pope and Peachy, Proc. Roy. Soc. 1903, 72, 7; Chem. Soc. Proc. 1900, 42, 116; Pfeiffer, Ber. 1904, 37, 4618; Shukoff, Ber. 1905, 38, 2691).

The tin halogen compounds form a number of double compounds with aliphatic and aromatic amines (Cook, Amer. Chem. J. 1899, 22, 435; Richardson and Adams, *ibid.* 446; Slagle, *ibid.* 1898, 20, 633).

Pyridine stanni-iodide $(C_5H_5N)_2H_2SnI_6$ is formed when an alcoholic solution of pyridine hydriodide is added to stannic iodide dissolved in alcoholic hydrogen iodide. It forms bluish-black glistening needles. The analogous *quinoline* salt $(C_9H_7N)_2H_2SnI_6$ forms black needles. Both these compounds decompose gradually, liberating iodine (Rosenheim and Aron, Zeitsch. anorg. Chem. 1904, 39, 170). Similar chlorides, bromides and alkyl derivatives have also been prepared (Pfeiffer, Annalen, 1910, 376, 310; *see* also Hayes, J. Amer. Chem. Soc. 1902, 24, 360).

A number of other organic compounds of tin have also been prepared (Fischer, Monatsh. 5, 426; Werner and Pfeiffer, *l.c.*; Thiele and Dimroth, Annalen, 1899, 305, 102; Pfeiffer and Lenhardt, *l.c.*; Dilthey, Ber. 1903, 36, 925; Rosenheim and Levy, *ibid.* 1904, 37, 3662; Rosenheim and Schnabel, *ibid.* 1905, 38, 2777; Weinland and Bames, *l.c.*; Pfeiffer, Annalen, 1910, 376, 285).

TIN PLATES. *History.*—Although the art of tinning brass and copper was well known to the Romans (*v. supra*), the production of sheet iron coated with tin, or 'tin plate,' is of a considerably later period. The art was probably of German origin, and existed in Bohemia prior to 1620. About this time the manufacture was introduced into Saxony, and speedily developed into a thriving industry. Unsuccessful attempts, with which M. Réaumur was connected, were made to introduce the manufacture into France. About 1670 an English company was formed to start a tin-plate works in this country, and Mr. Yarranton was sent to Germany to learn the art. Works were started at Pontypool, and met with some success, but were stopped, owing to the grant of a patent for the manufacture to E. Hemming in 1691. Works were, however, once more started in 1720 at Pontypool, and these were gradually followed by others, particularly in South Wales, which gradually became the most important seat of the manufacture in the world. In the earlier processes of manufacture the plates were hammered by hand from iron made in the charcoal hearth, while the surface was cleaned from scale by immersion for several days in sour barley-water, instead of for a few minutes in dilute sulphuric acid, as at present.

In 1728, the *rolling* of sheets was introduced by Hanbury, of Pontypool, while sulphuric acid was substituted for barley-water in 1806. The rolling of tin plates as they leave the tin pot, which saves metal and improves the surface, was introduced by Morewood (who took out many patents for coating metals) in 1866, since which time a great variety of machines have been introduced for use in the tinning process.

Pickling machines have superseded hand labour, while iron made in the old-fashioned open-hearth refinery (or puddling furnace for second qualities) has been generally replaced by steel. Siemens' steel was used about 1875, Bessemer steel about 1880, and basic steel was introduced a few years later (*v.* P. W. Flower, Origin and Progress of the Manufacture of Tin Plates, J. Iron and Steel. Inst. 1886; C. Vogel, Stahl und Eisen, 29, 1097).

The M'Kinley Tariff, which came into force on July 1, 1891, led to a rapid development of the tin-plate industry in the United States, and a corresponding depression in South Wales. Other markets for Welsh tin plates were, however, gradually found, so that the industry has more than made up for the ground lost.

Production of tin plate. The metal used for rolling into sheets was formerly, as above stated, wrought iron of special quality, which was made in refineries using only charcoal. At present very mild steel is employed, Siemens' steel being in most demand for this purpose. The bars are cut into suitable lengths, and each length is heated to redness, and then passed through 'chilled' rolls until its length is about doubled; the plate is then folded across the middle, re-heated, and again rolled. The reheating, folding over, and rolling is repeated until a sheet of the proper thickness is obtained, sometimes as many as thirty-two thicknesses being rolled together as one piece in this way. The sheets are then cut to size with shears and separated, when they should part readily if the operation thus far has been successfully conducted. The 'rough black plates' so produced should be free from streaks or 'spilly' places and should be uniformly coated over with a black scale of oxide. This is now removed by 'pickling' in warm dilute sulphuric acid for about 20 mins., and by subsequent washing and rubbing with sand and water. The sheets are next annealed in wrought-iron boxes, which are usually about 2 ft. square, but vary in size; the upper part is in the form of a bell for ready removal, and to prevent the entry of air the joint is stopped by being covered with sand. The annealing requires about 10 hours, and is conducted in a large furnace maintained at a cherry-red heat. The pots are then withdrawn and allowed to cool, after which the sheets are cold-rolled, to improve the surface and give the smoothness and uniformity which is necessary to produce a good tin plate. The cold-rolling renders the plates somewhat hard, and they are therefore annealed once more, usually in cast-iron pots, as it is not necessary in the second annealing to use so high a temperature or as long a time as in the first case. The sheets are now finally pickled in weaker sulphuric acid than was used in the previous pickling, and after being again rubbed with sand are immersed in water preparatory to tinning.

The tinning apparatus, or 'stow,' varies somewhat with the size and quality of the plates; with very large plates the bath of tin is contained in a basin-shaped pot, while for large sizes and ordinary qualities the plates are manipulated entirely by machinery during the tinning process.

The form of apparatus which was general in S. Wales until nearly the end of the nineteenth century, and which is still occasionally employed for purposes where a specially good tin plate is required to withstand atmospheric and similar influences, consists of five baths or pots, called respectively (1) the grease pot, (2) the tin-man's pot, (3) the washing pot, (4) the dipping pot, (5) the grease pot. Formerly two other pots were used, but these have been rendered unnecessary by the introduction of rolls. The grease pot contains melted grease, such as tallow or palm oil, and in this the sheets are dipped until all moisture has been removed and they are uniformly coated with grease. They are next dipped into the tin pot, which contains melted tin covered with a layer of grease, the latter being now usually replaced by a bath of zinc chloride or 'killed spirits.' The sheet now receives its first coating of tin, which, however, is not perfect, and to complete the tinning the sheet is dipped into the first compartment of the washing-pot, where it remains until a uniform coating is produced. The plate is now taken out and rapidly examined by the workman, who wipes over the surface with a brush, and to remove the marks of the brush rapidly dips the plate into the second compartment of the same pot, which contains the best tin, and then transfers it to the grease pot, where it passes through a pair of rolls, which squeeze off the excess of tin and improve the surface. Formerly the plate remained for about 10 mins. in the grease pot, during which time the excess of tin drained off. The plate was afterwards transferred to the 'cold pot,' after which the lower part was inserted in the 'list' pot, which contains a little tin at a comparatively high temperature, and which rapidly removes the thick edge of tin which had accumulated at the bottom of the plate. The plates, after coating with tin, are then cleaned from grease, usually by rubbing with bran and finishing with the woolly skin of a sheep; they are afterwards separately examined for defects, and, after classification, are packed in the familiar flat wooden boxes and branded for market (*v.* E. Trubshaw, J. Iron and Steel Inst. 1883, i. 252).

For a description of the process of manufacture of tin plates in Germany, which does not materially differ from that above described, *v.* Dingl. poly. J. 250, 231.

In modern tin-plate works mild steel bars are reheated and rolled into 'black plates' by passing successively through two pairs of rolls for 'roughing' and 'finishing' respectively. In the United States sometimes only one pair of rolls is used; or two pairs of finishing rolls may be served by one pair of roughing rolls. The plates, after being separated, are pickled in diluted sulphuric or hydrochloric acid with the aid of pickling machines; they are then annealed under cover in iron or steel boxes, cold rolled, re-annealed at a lower temperature and again pickled, this time in weaker acid. The plates are then swilled in water and introduced, without drying, into the tinning machine. Of such machines there are various modifications. A typical form consists of two divisions connected with each other at the lower part of the pot which contains molten tin. The tin in the first division is coated with a tinning flux of zinc chloride, while that in the second division is covered with hot grease. The plate passes through the flux into and through the tin, emerging through the grease, and passing through rolls which remove the surplus tin, and give a smooth, bright, and even surface. For further details and drawings, *see* G. B. Hammond, The Manufacture of Tin Plates, J. Iron and Steel Inst. 1897, 2, 24.

The occurrence of blisters in the thin sheets of steel used in the manufacture of tin plates is not infrequently a cause of considerable trouble. The origin of these has been studied by E. F. Law (J. Iron and Steel Inst. 1906, 1, 134) who concludes that oxidised steel will give rise to blistered sheets, and the defect is more likely to arise with Bessemer, than with open hearth steel. Brittleness in sheets may arise from excess of sulphur or phosphorus. In metal of good chemical purity a peculiar form of weakness, sometimes called "rectangular brittleness," may result from annealing at an improper temperature, or for too long a time. T. T.

TIN PYRITES *v.* Stannite.

TIN SALTS or **TIN CRYSTALS.** *Stannous chloride v. Tin salts and oxides*, art. Tin.

TIN STONE. *Native oxide of tin v.* Cassiterite.

TINTOMETER *v.* Colorimeter.

TIN WHITE COBALT. *Smaltine, Cobalt arsenide v.* Cobalt.

TITANIC IRON-ORE *v.* Ilmenite.

TITANITE *v.* Titanium.

TITANIUM. Sym. Ti. At. wt. 48·1.

Titanium is not found in the free state, but occurs as oxide in three minerals of different crystalline form: *rutile, anatase*, and *brookite*. It is found as *titaniferous iron ore* or *ilmenite* $(FeTi)_2O_3$, and in smaller quantities as *sphene* or *titanite* $CaTiSiO_5$, *perofskite* $(CaFe)TiO_3$, *schorlomite* $Ca(TiFe)SiO_5$, and *keilhauite* $CaY(TiAlFe)SiO_5$. It occurs in magnetic iron ores, and is thus frequently found in slags and pig iron; and in other minerals, in soils, clays, certain mineral waters, and in the sun's atmosphere (Barnes, J. Soc. Chem. Ind. 1896, 421; Rieke, *ibid.* 1908, 901; Becker, Zeitsch. Kryst. Min. 1903, 38, 317; Hall and Smith, Chem. Zentr. 1905, ii. 1161). The presence of titanium oxide in clays considerably reduces their refractibility. Titanium is said to be diffused throughout all primitive granite rocks (Dieulafait).

It has also been found in human and in ox flesh and bone (Baskerville, J. Amer. Chem. Soc. 1899, 21, 1099); in the ash of many plants (Wait, *ibid.* 1896, 18, 402; Lippmann, Ber. 1897, 30, 3037); and in many peats (Baskerville, *l.c.* 402). It is more abundant in nature than has hitherto been supposed, but it is only within the last few years that the metal and many of its compounds have become important industrially.

Titanium can be extracted from its oxide by electrolysing a solution of the latter in dry halogen salts of the alkaline earth metals heated to moderate redness. After cooling, the titanium is separated from the electrolyte by lixiviation with water and with dilute hydrochloric acid (Fr. Pat. 344099, 1904; J. Soc. Chem. Ind. 1904, 1098; *cf.* also Moissan, Eng. Pat. 2073, 1895; Sternberg and Deutsch, Eng. Pat. 13117, 1893; Borschers, U. S. Pat. 930344, 1909; J. Soc. Chem. Ind. 1909, 986). In a somewhat impure form it can be obtained by the reduction of potassium titanium fluoride with sodium (Weiss and Kaiser, Zeitsch. anorg. Chem. 1910, 65, 345). Very pure titanium has been obtained in moderately large quantities by heating pure titanium tetrachloride with about half its weight of sodium in a steel bomb to a low red heat (Hunter, J. Amer. Chem. Soc. 1910, 32, 330).

Titanium has the appearance of polished steel. It is hard and brittle in the cold, but can be readily forged when raised to a low red heat. It has sp.gr. 4·50 and melts at 1800°–1850° (Hunter); (*see* also Moissan, Compt. rend. 1906, 142, 673).

Titanium burns in oxygen and in the halogens, dissolves readily in sulphuric or hot concentrated hydrochloric acid, more slowly in nitric acid, and decomposes steam at 700°–800°.

Titanium readily forms alloys with various metals; some of those with iron having been employed for the manufacture of pencils for arc lights (Ladoff, J. Ind. Eng. Chem. 1909, 711).

Filaments of metallic titanium having a high melting-point and high resistance, and as used for incandescent electric lamps, are manufactured by treating titanic oxide with ammonia in the cold. The product is heated in a vacuum to 1200°, and is then mixed with an organic binding material such as a solution of casein in ammonia. The mixture is formed into threads and then heated in an electric furnace to 1200°. Finally the filament is subjected to the action of a high tension electric current in a vacuum (Trenzen, Eng. Pat. 14852, 1908; J. Soc. Chem. Ind. 1909, 877).

Titanium is used in metallurgy, its addition to steel increasing greatly the transverse strength and elasticity of the steel (Ladoff, *l.c.* 642; Venator, Stahl und Eisen, 1910, 30, 650).

A protective coating on iron and steel is said to be formed by mixing a titanium ore with 10–50 p.c. of asphalt, and if the product is to be used as a paint, adding turpentine. These coatings can also be formed by heating the metal to be treated with a layer of titanic mineral mixed with carbonaceous material in a furnace for several hours (Johnson, Eng. Pat. 15500, 1893; J. Soc. Chem. Ind. 1893, 1046).

Compounds of titanium. Titanium forms four oxides. The *monoxide* TiO forms black prisms, obtained by heating the dioxide in the electric furnace, or with magnesium powder (Winckler, Ber. 1890, 23, 2658; Moissan, Compt. rend. 1892, 115, 1034; J. Soc. Chem. Ind. 1909, 982). The *sesquioxide* Ti_2O_3 (Moissan, Compt. rend. 1895, 120, 290; Braun, Min. Mag. 1892, ii. 37) is obtained by strongly igniting the dioxide in hydrogen and allowing the product to cool in this gas. In sulphuric acid it forms a violet solution, this being the characteristic colour of all the solutions of trivalent titanium compounds. The corresponding *hydroxide* is obtained by digesting a solution of titanic acid in hydrochloric acid with metallic copper at 20°–40°, or by treating the trichloride with alkalis. The sesquioxide and the corresponding salts are readily oxidised to the dioxide or the trioxide and their salts (Manchot and Richter, Ber. 1906, 39, 320, 488).

Titanium dioxide TiO_2 is the most important of the four oxides. It is trimorphous, occurring as the three distinct minerals mentioned above. It can be obtained by the decomposition of aqueous titanium chloride by ammonia or by fusing rutile with three times its weight of potassium carbonate.

Titanium oxide can be prepared by mixing crushed ilmenite or other titanium ore with carbon and heating to about 1800°. The resulting mass is crushed and the iron is removed by magnetic separation and treatment with acid (U. S. Pat. 921686, 1909; J. Soc. Chem. Ind. 1909, 657).

Amorphous titanium dioxide is a white, tasteless powder which becomes lemon yellow when gently heated, and brown when ignited strongly. It has a sp.gr. 3·89–4·25. It is insoluble in water and dilute acids, resembles silicon dioxide closely in chemical properties, and when fused with alkalis or alkali carbonates forms the titanates.

Titanium oxide is used as a mordant, and in at least two cases it has an advantage over alumina; thus alizarin yellow produces with titanium as bright but a much faster colour than with alumina, whilst the scarlet obtained from alizarin orange on a titanium mordant is the fastest scarlet that can be obtained on wool.

For this purpose the titanium mordant must be freed from iron, and this can be done by dissolving freshly precipitated titanium hydroxide, containing iron, in tartaric acid, making alkaline with ammonia and precipitating the iron by the addition of the requisite amount of ammonium sulphide. The filtered solution is then warmed until most of the free ammonia has been expelled (Barnes, J. Soc. Chem. Ind. 1899, 15).

According to Sabatier and Maille (Compt. rend. 1910, 150, 823) the dioxide forms a very efficient catalyst in the esterification of acetic acid.

Like silicic acid, titanic acid forms a number of hydrates known as ortho- and meta-titanic acids (Wagner, Ber. 1888, 21, 960; Pfordten, Annalen, 1887, 237, 213; Tamann, Zeitsch. anorg. Chem. 1905, 43, 370: Bornemann and Schirmeister, Chem. Zentr. 1910, ii. 1870). Many titanates are known.

Titanium peroxide TiO_3 (Classen, Ber. 1888, 21, 370) resembles hydrogen peroxide very closely in its reactions in solution. Faber (Zeitsch. anal. Chem. 1907, 46, 277) has prepared the hexavalent acetate and phosphate

$$Ti(OH)_4PO_4,$$

both of which are stable at low temperatures, but, particularly the acetate, are explosive on heating. Hypertitanates of potassium and sodium have also been prepared (Melikoff and Pissarjewsky, Ber. 1898, 31, 678).

Halogen compounds. **Titanium tetrachloride** $TiCl_4$ can be obtained readily by passing dry chlorine over a mixture of the dioxide with carbon; by passing the vapour of chloroform over titanium dioxide (Renz, Ber. 1906, 39, 249), and by heating the latter with sulphur monochloride (Hall, J. Amer. Chem. Soc. 1904, 26, 1235; Bourion, Ann. Chim. Phys. 1910, [viii.] 20, 547; *ibid.* 21, 49).

Titanium tetrachloride is best prepared from industrial ferro-titanium by treating the latter with hydrochloric acid to remove most of the iron. It is then levigated to remove titanic anhydride, and after drying the mass is introduced into a porcelain tube, heated to dull redness, and subjected to the action of a current of dry chlorine. The ferric chloride is separated by filtration, and the filtrate is fractionally distilled when the pure substance is obtained. It boils at about 136°, is colourless, and does not fume in air (Vigouroux and Arrivaut, Compt. rend. 1907, 144, 485).

The tetrachloride can also be prepared from rutile by igniting the latter with aluminium and then heating the mixture in a current of chlorine (Ellis, Chem. News, 1907, 95, 122).

It is a mobile, transparent, colourless liquid of sp.gr. 1·7604 at 0°/4° (Thorpe) which solidifies at −23° and boils at 136·4° under 760 mm. pressure (Thorpe). It is decomposed by an excess of water yielding titanic acid and combines with ammonia, forming a number of solid addition compounds (Rosenheim and Schütte, Zeitsch. anorg. Chem. 1901, 26, 239; Stähler and Wirthwein, Ber. 1905, 38, 2618). When the latter are extracted with liquid ammonia, dark yellow *titanamide* $Ti(NH_2)_4$ is formed. Titanium tetrachloride, like stannic chloride, yields a large number of crystalline compounds with other chlorides (Rosenheim and Schütte, *l.c.*; Ruff and Ipsen, Ber. 1903, 36, 1777).

Titanium trichloride $TiCl_3$ is formed when a mixture of titanium tetrachloride vapour with hydrogen is passed through a red-hot tube (Georges and Stähler, Ber. 1909, 42, 3200), and can be prepared by electrolysing a solution of the tetrachloride and then evaporating the solution to the sp.gr. 1·5 at 60°–70° (Spence, U. S. Pat. 723217, 1903; J. Soc. Chem. Ind. 1903, 495, 628; D. R. P. 154542). As prepared by the latter process, it forms violet crystals of the composition $TiCl_3,6H_2O$, which decompose into the tetra- and di-chloride on heating, the latter also being formed when the trichloride is heated in hydrogen (Georges and Stähler, *l.c.*). The trichloride is a powerful reducing agent. It liberates sulphur from sulphurous acids, many metals, such as gold, silver, mercury, and copper from solutions of their salts, and reduces nitric acid and nitrates to ammonia. It reduces ferric salts quantitatively to the ferrous condition, organic nitro compounds to amines, and can be employed in the analysis of many dyes (Knecht, Ber. 1903, 36, 166; Knecht and Hibbert, *ibid.* 1549; *ibid.* 1905, 38, 3318; 1907, 40, 3819). This reducing property has also been made use of in cloth printing (D. R. P. 138503; Frdl. 1902–4, 477). Titanium trichloride forms double compounds with the chlorides of rubidium and caesium (Stähler, Ber. 1904, 37, 4405), and also with nitrogen sulphide (Davis, Chem. Soc. Trans. 1906, 1576).

Titanium dichloride $TiCl_2$, prepared as above, is a hygroscopic light-brown powder.

Titanium tetrabromide (Ruff and Ipsen, *l.c.*), and *tribromide* (Stähler, *l.c.*), the *triiodide* (Stähler, *l.c.*), *tetra-iodide* and the *diiodide* (Defacqz and Copaux, Compt. rend. 1908, 147, 65), the *tetra-* and *tri-fluorides* (Ruff and Ipsen, *l.c.*; Ruff, Plato and Graf, Ber. 1904, 37, 673), and a number of *alkali titanofluorides* (Marchetti, Zeitsch. anorg. Chem. 1895, 10, 66; Piccini, *ibid.* 438; Ebler and Schott, J. pr. Chem. 1910, [ii.] 81, 552) have been prepared.

Titanium forms three *sulphides* TiS_2, Ti_2S_3, and TiS (Müller, Chem. Zentr. 1910, ii. 1195), and also a chlorosulphide.

Titanium sesquisulphate $Ti_2(SO_4)_3,8H_2O$ is obtained when the metal is dissolved in dilute sulphuric acid. It is decomposed by heat and forms alums and double salts with the alkali sulphates.

The electrolytic reduction of many organic compounds is greatly facilitated by the addition of a small quantity of a titanium salt, such as the sulphate (D. R. P. 168273; Frdl. 1905-7, 115). Titanous sulphate is also recommended for detecting copper in dyed fabrics (Knecht, J. Soc. Dyers, 1904, 20, 97).

Titanous sodium sulphate $Ti_2Na_2(SO_4)_4,5H_2O$ is obtained by electrolysing a solution containing titanic sulphate, sodium sulphate, and sulphuric acid. The electrolysis is carried out with a low-current density in a lead-lined vessel, the solution being finally evaporated to a sp.gr. of 1·145, when the salt crystallises out.

It is a powerful reducing agent, and can be applied in the preparation of other titanous salts (Peter Spence and Sons, D. R. P. 149602, 1904).

Titanium disulphate $Ti(SO_4)_2,3H_2O$ forms double salts with the sulphates of the alkalis and alkaline earths (Weinland and Kühl Zeitsch. anorg. Chem. 1907, 54, 253). A number of basic sulphates (Blondell, Bull. Soc. chim. 1899, [iii.] 21, 262; Roseheim and Schütte, *l.c.*) and titanosulphuric acid (Reichard, Chem. Zeit. 1904, 28, 16) have also been prepared.

Titanium forms a number of nitrides and also a chloro- and bromo-nitride (Ruff and Eiser, Ber. 1908, 41, 2250; J. Soc. Chem. Ind. 1908, 809; Ruff, Ber. 1909, 42, 900). The mononitride Ti_2N_2 is a bronze yellow mass of sp.gr. 5·18, and is hard enough to cut rubies and diamonds (Moissan, Compt. rend. 1895, 120, 290).

According to Shukoff, however (J. Russ. Phys. Chem. Soc. 1910, 42, 40), titanium only forms solid solutions with nitrogen, but no definite compounds.

Titanium also forms a *carbide* (Shimer, Chem. News, 1887, 55, 156; Moissan, *l.c.*; and Compt. rend. 1897, 125, 839); a *cyanonitride* $Ti(CN)_2{\cdot}3Ti_3N_2$ (Wohler, Annalen, 1850, 73; *ibid.* 34, 74, 212; Franck, Chem. Zeit. 1897, 21, 520; J. Soc. Chem. Ind. 1908, 809); and a *silicide* $TiSi_2$ (Hönigsmid, Compt. rend. 1906, 143, 224; J. Soc. Chem. Ind. 1909, 249).

Soluble double pyrophosphates of titanium and alkali are prepared by mixing together alkali pyrophosphates and basic titanium sulphate (Barnes and Spence, Eng. Pat. 6329, 1906; J. Soc. Chem. Ind. 1907, 93).

Titanium phosphide TiP forms a brittle mass with a metallic lustre. It burns when heated in air, is a conductor of electricity, is insoluble in dilute and in concentrated alkalis and acids (Gewecke, Annalen, 1908, 361, 79).

Titanic acid forms crystalline *thiocyanates* of the type $K_3TiO(SCN)_4H_2O$ and double salts with pyridine $(C_5N_5H)_2H_2TiO(SCN)_4$, and quinoline (Rosenheim and Cohn, Zeitsch. anorg. Chem. 1901, 28, 167).

Double fluorides of titanium with some alkaloids are described by Schaeffer (J. Amer. Chem. Soc. 1908, 30, 1862).

Complex azo- salts of titanium have been prepared by Mazzucchelli and Pantanelli (Gazz. chim. ital. 1910, 40, i. 666). Other titanium organic compounds are described by Dilthey (Ber. 1904, 37, 588; Annalen, 1906, 344, 300), Rosenheim and Schnabel (Ber. 1905, 38, 2777), Grossmann (Chem. Zeit. 1906, 30, 907), Muzzucchelli (Atti. R. Acad. Lincei, 1907, [v.] 16, ii. 265), Fenton (Chem. Soc. Trans. 1908, 1064).

The possibility of using titanium compounds in dyeing processes was first demonstrated by Barnes in 1877, but has only recently been applied by manufacturers. The salts sued are: the sulphate, chlorides, fluoride, oxalate, tartrate, lactates, and the double alkali derivatives of these salts. The salts for this purpose are obtained by the following process:—

The ore is melted with sodium hydroxide and the mass is lixiviated with water; the residue is then washed free from alkali, dissolved in hydrochloric acid, and the solution is treated with alkali to precipitate titanium as hydroxide. The product is freed from iron by the addition of sodium sulphide, washing the precipitate and treating it with sulphurous acid. It is then converted into titanium oxalate by treatment with ammonium oxalate and oxalic acid (Erben, Chem. Zeit. 1906, 30, 145; *cf.* also Dreher, Eng. Pat. 1835, 1903; J. Soc. Chem. Ind. 1904, 18; Spence, *ibid.* 1900, 246).

The *lactates* are conveniently prepared by dissolving titanic acid in hydrochloric acid and pouring the solution obtained into a warm solution of an alkali or alkaline earth lactate (Dreher, Färber Zeit. 1902, 13, 293; D. R. P. 149577; Frdl. 1902–4, 43; J. Soc. Chem. Ind. 1902, 988, 1245; 1903, 908).

The soluble salts of titanium, such as the oxalate, are very efficient fixing agents for the tannates of the basic colours, the results obtained being as good as, and in many cases better than, those obtained with antimony. For this purpose it is unnecessary to purify the titanium salts from iron (Barnes, J. Soc. Chem. Ind. 1899, 15).

Titanium tannate washed free from sulphate and chlorides, and dissolved in warm aqueous oxalic or tartaric acid, is an excellent dye for cotton, the shade varying with the sp.gr. of the solution. The solution of titanium tannate can also be employed as a further fixing and modifying bath after dyeing, the colours becoming faster and more yellow after such treatment. It also serves as an excellent fixing agent for the Janus colours which have been dyed substantively. Very good colours are also obtained with methylene blue, rhodamine, and aniline black (Barnes, *l.c.*; Kearns and Barnes, Eng. Pat. 8589; J. Soc. Chem. Ind. 1899, 491; Erban, Chem. Zeit. 1906, 30, 145).

A solution containing a titanium salt gives, with tannic acid, an orange precipitate; with gallic and pyrogallic acids, orange or brownish-yellow solutions; and with salicylic acid a pale-yellow coloration: a yellow to deep orange colour is also produced by hydrogen peroxide; these colours are imparted to wool when the latter is steeped in the hot solutions (Barnes, J. Soc. Chem. Ind. 1896, 420; 1897, 238; Eng. Pat. 5712).

The oxalate, tartrate, titanium potassium oxalate, titanium-tanno-oxalate, titanium sodium sulphate and titanous chloride can be used with good results in dyeing and mordanting silk. The titanium mordants are also useful in the chrome developing colours, and in the after treatment of silk previously dyed with anthracene yellow or brown or alizarin colours. For this purpose titanium potassium oxalate or titanium sodium sulphate are best used (Hurst, J. Soc. Dyers, 1903, 19, 105; Barnes, *l.c.*).

Titanium salts unite with the tannin matter of leather to form on the fibre a yellowish-brown titanium tannate, which is very fast to light and to the action of soap. On account of its cheapness, potassium titanium oxalate is the most applicable. It is exceedingly soluble in hot water and can be applied to tanned leather either in the dye-bath or with a brush. The mode of application and the previous and subsequent treatment of the leather depend on the quality of the latter, whilst the shade of colour obtained, which varies from bright yellow to a reddish-brown, depends on the nature of the tannage and on the amount of titanium salt used. The basic colours especially give much fuller and richer shades with titanium than without (Lamb, J. Soc. Chem. Ind. 1901, 1111; U. S. Pat. 722857, 1903; Dreher, J. Soc. Chem. Ind. 1902, 771; 1903, 294; 1904, 71; Eng. Pats. 9556, 1901; 27597, 1902; Stiasnky, J. Soc. Chem. Ind. 1902, 1329; Erben, *l.c.*).

According to Barnes (*l.c.*) titanium tannate can also be used effectively as a pigment in water-colour drawings, the colour depending upon the conditions of preparation of the pigment and varying from brick-red to almost pure yellow. Titanium salts are also said to be employed in the manufacture of artificial teeth and in colouring porcelain (Ladoff, *l.c.*; Barnes, J. Soc. Chem. Ind. 1896, 421). Z. K.

TITANIUM GREEN. Titanium ferrocyanide, prepared by adding potassium ferrocyanide to a solution of hydrated titanic oxide in hydrochloric acid, has been suggested as a substitute for Schweinfurth green and other arsenical pigments (Elsner, Dingl. poly. J. 905, 130; Gentele, *ibid.* 140, 238).

TITRATION *v.* ANALYSIS.

TIZA. A local South American name for ulexite (*q.v.*).

TOAD'S EYE. *Native oxide of tin v. Tin salts and oxides*, art. TIN.

TOBACCO. The botanical order of the *Solanaceae* includes many well-known plants which are extensively cultivated because certain portions of them are of great utility to the human race. The tuber of the potato and the fruit of the tomato are food substances of great value and of almost universal consumption. Other genera of the order, however, afford instances of cultivation simply for the production of foliage; the dried leaves of the thorn-apple (*Datura Stramonium* [Linn.]) are sometimes smoked as a remedy for asthma. The most important plants of this class, however, belong to the genus *Nicotiana*, and their dried leaves are known as tobacco. The etymology of the word 'tobacco' is somewhat obscure; the geographical origin assigned to it by tracing it either from Tobago, an island in the West Indies, or from Tabasco, an island in the Gulf of Mexico, is probably incorrect. When the Spaniards first visited San Domingo they found that the natives used a peculiar contrivance for inhaling the smoke of burning tobacco leaves. This instrument was called a 'tabaco,' and was shaped like a Y with the arms so close together that they could be inserted up the nostrils, and it is highly probable that the word tobacco thus originated.

Upwards of 40 species of the genus *Nicotiana* have been described, but many of them are simply modifications resulting from the influence of soil and climate on the chief species. *Nicotiana Tabacum* (Linn.), the most important member of the genus, is a fine plant, indigenous to America, where it grows from 6 to 9 ft. high. The stem is slightly viscous, and the leaves, which are oblong or lanceolate in shape, are attached alternately, and surround the stem in the form of a spiral (of which the ninth leaf overhangs the first, the tenth the second, and so on). The distance between the leaves is usually about 2 ins. Characteristic soft downy glandular hairs cover the stem and the under surface of the leaves, and these are of great service in the identification of tobacco by the microscope. The flowers have funnel-shaped corollas, about 2 ins. long, of a rose or pinkish colour, and are produced in large terminal clusters: the seed pods have two valves, and the seeds are very small and numerous. Modifications in the type have resulted in the production of several varieties of this species, differing chiefly in the size of their leaves. The two principal groups now recognised are *Nicotiana Tabacum*, var. *macrophylla*, or 'Maryland tobacco,' comprising stalked and stalkless forms, and *Nicotiana Tabacum*, var. *angustifolia*, or 'Virginia tobacco.' The finest growths of Cuba, Manila, and Turkey (including Latakia), are now attributed to a form of the stalked Maryland tobacco. Under the name of Shiraz tobacco, *N. persica*, a very fine variety, is cultivated in Persia; but the plant is probably a form of *N. Tabacum*, obtained by cultivation of seed derived from a Brazilian variety. Of the remaining species, *Nicotiana rustica* (Linn.) is the most important. It is of hardier constitution and dwarfer habit than the preceding species, and the flowers are also of a lighter colour. It is cultivated largely in Germany, Hungary, and in the East Indies, and includes the common Hungarian and Turkish varieties.

The use of tobacco for smoking purposes is supposed to have originated among the North American Indians. When America was first discovered, and afterwards when fresh portions of the continent were explored, the practice was found to be prevalent among all the native tribes, and its introduction into Europe very soon followed. The plant was first cultivated in Spain early in the sixteenth century, and was introduced into France and Italy about the year 1560. It attained considerable fame as a medicinal herb, and was at first regarded with universal favour. Sir Walter Raleigh is generally credited with having introduced its cultivation into the British Isles in the year 1586, but plants are said to have been brought to England by Sir John Hawkins in the year 1565. The habit of smoking soon became general, but this use of the plant met with a considerable amount of opposition, not only in England, but also throughout Europe. Nearly the whole of the early literature on the subject was written in an antagonistic strain. Kings' counterblasts, Popes' anathemas, Sultans' decrees and even violent punishments failed to check the growing habit, and plantations sprang up, not only in the New England States, but also all over the United Kingdom. In the year 1604 the tax on the imported article was raised from 2*d*. per lb. to 6*s*. 10*d*. per lb., and English planters were forbidden to produce more than one hundredweight of the leaf. Shortly afterwards the pre-emption of tobacco was made a royal monopoly, and the King enjoined the plucking up of all tobacco found growing in England and Ireland. In the years 1652, 1660, and 1663, Acts were passed prohibiting the cultivation of tobacco in England and Ireland, and these Acts were extended to Scotland in the year 1782. The prohibition as regards Ireland was removed in the year 1779, but was subsequently reimposed in the year 1831. Notwithstanding these measures, the cultivation of tobacco in England did not really cease until the year 1782, when some planters in the vale of York were imprisoned and fined in the sum of £30,000.

Culture. The tobacco plant, though essentially tropical, can, with suitable modifications in the cultural details, be grown successfully in temperate climates. It is cultivated for commercial purposes chiefly in the United States, Cuba, Mexico, Brazil, Paraguay, the Dutch Indies and North Borneo, Australia, India, China, Burmah, the Philippines, Persia, the Transvaal, Rhodesia, the Levant, Greece, Hungary, Germany, Russia, France, and Holland, and is now being grown on a small scale in the United Kingdom. Cigar leaf is grown in Cuba, the East Indies, North and South America, Rhodesia, and Germany; tobacco for pipe smoking in the United States, the Levant, Germany, the Transvaal, Nyassaland, Australia, China, Java, &c.; tobacco for cigarettes in the United States, the Levant, Greece, &c. In the United States, several types of leaf are grown, of which the principal are the Seed leaf and Florida varieties of Cuba and Sumatra tobacço for cigars; White Burley; the Heavy Shipping or dark tobacco of Kentucky, Virginia, and Maryland; the Yellow tobacco of Carolina and Virginia; and the Perique of Louisiana. A spangled type of yellow tobacco is grown also in Ohio. Seed leaf requires a strong, highly-manured soil, to promote a rapid growth, so that the plants may be harvested when expansion of the leaves ceases, and the process of granulation and secretion of the gummy substances begins. White Burley flourishes in a highly fertile disintegrated limestone, while heavy shipping tobacco thrives best on ferruginous clayey soils. Yellow tobaccos need a sandy, porous, sterile soil, to which just sufficient fertilisers (superphosphate, potash, and nitrogenous) have been added to promote summer growth; in the autumn the plant's declining vitality causes the leaves to turn more and more yellow until the tint desired is reached, which is afterwards fixed in the curing process. Perique is grown on the low-lying lands, black with humus, in the swampy districts of Louisiana. Climate has a great influence on the flavour, but the texture of the leaf depends largely on the nature of the soil in which the plant grows. The northern varieties, for example, planted in the Southern States gradually change in character; the plants ripen earlier and the leaves assume a lighter colour and diminish in size but increase in thickness and sweetness.

The seed is sown in February, March, or April, in seed beds, composed of a light friable soil prepared some time beforehand, and a brush heap is burned on the ground prior to sowing to destroy harboured insects. The young plants are raised either in hot beds, or in cold frames protected by plant-muslin, according to the locality. In the three months from April to June, when the plants are about 6 ins. high, they are transplanted into well ploughed soil, thrown up in ridges; and if the weather is dry, they are watered in. A space of from 1½ to 3 ft. is allowed between each plant in the rows, which are made from 3 to 4 ft. apart. The constant removal of suckers from the plants ('suckering'), frequent harrowing of the soil, and destruction of weeds and insect pests are necessary. In Turkey and other Eastern countries, where small leaves are desired, and the buds and flowers are also used, 'topping' is not practised, but the larger growths of the United States, &c., usually require this treatment when the first bloom begins to show. Ten to a dozen leaves in the case of heavy shipping tobacco, and 16 to 18 leaves in the other varieties, are allowed to remain on the stem, and the increase in their leaf surface they thus show may be as much as 50 p.c., when compared with leaves of normal size. Seed leaf requires from 2 to 3 weeks after this operation to ripen, yellow leaf and Burley take a month, and heavy shipping tobacco 2 or 3 weeks longer. An abnormal amount of organic matter accumulates in the cells of ripe tobacco leaf, owing to the 'topping' and 'suckering' of the plant. The continuous accumulation of nicotine, oxidising enzymes and acids which takes place in the cells finally causes the chlorophyll granules to acquire a yellowish colour. The change from the normal deep green tint of the leaf is very noticeable to the experienced eye, and indicates that the time for harvesting has arrived. The constituents of the cells having fulfilled their functions are at this stage going back to the stem to be transferred thence to the upper leaves, to be used for other purposes in the economy of the plant. Compared with the young leaf, the ripe leaf has a density half as high again, and contains about 2¼ times as much matter soluble in boiling water. White Burley and seed leaf are air cured in houses that can be ventilated at will: this operation requires from 6 to 8 weeks. An alternating change from the moist to the dry condition of the leaves takes place according to atmospheric conditions as the curing proceeds. Yellow leaf is cured by artificial heat, distributed by flues in air-tight barns. The temperature is maintained at 80° to 90°F. for 18 to 36 hours for the leaf to acquire the proper colour, and the heat is then raised by 5° to 10° at a time, about every 2 hours, to 115° to 120°F., and maintained at this point until the leaf is properly cured. The curing of the stalks is then effected by raising the temperature hourly by 5° to 10° to about 160° to 175°F. The whole operation takes about three days. Heavy shipping tobacco is hung on scaffolds or in the barns for some days to become yellow, and the curing is completed by open log-fires, kindled directly under the tobacco and gradually increased in size. In India, Ceylon, and other Eastern countries, sun-curing is sufficient; but in places where resort to artificial heat is necessary, it is essential that the increase of heat should be at first very gradual, as the object is not so much to dry the leaf as to fix as far as possible its qualities as regards colour, strength, elasticity and flavour. A fresh leaf subjected to a high initial temperature retains its green colour, whereas by slow drying the tint produced will vary from shades of yellow to brown. The proper fixing of the colour of the leaf is of great financial importance to the curer. The leaves, except those of the yellow varieties which are harvested as they ripen, are not usually removed from the stems prior to curing. Perique tobacco undergoes a special process of curing. After the leaves in the drying-houses have acquired a brown tint they are twisted into rolls containing about 30 leaves; these rolls are packed into boxes holding about 50 lbs. and heavy pressure is applied; the rolls are then slightly opened out and exposed to the air to aerate the exuded juices and, when these are re-absorbed, again subjected to pressure. This operation is repeated daily for about 10 days, and at longer intervals for some 3 months, with the result that the tobacco acquires a glossy black colour, and a rich characteristic spirituous odour. In Florida, cigar leaf is now grown from Cuba and Sumatra seed, but success was only achieved by making considerable changes in the ordinary methods of cultivation. The plants are placed closer together, about 14 ins. apart; the Cuban varieties are topped high, but the Sumatra kinds are allowed to bloom. Each plant yields from 18 to 30 suitable leaves which are primed off as they ripen. The discovery that plants shaded by trees were far superior to those grown in the open fields, led to the adoption of artificial shading, which has also been tried with success in Cuba, Porto Rico, and Connecticut.

Preparation for the market, which involves the grading, fermentation, and ageing of the tobacco, is usually managed by the packers and not by the farmers. Various enzymes occur in ripe tobacco leaf, which are capable of causing the oxidation of the cell-contents, and favourable conditions during the curing process promote their further development. They manifest increased activity during the fermentation, and the development of the aroma which takes place at this stage is believed to be due to the chemical changes resulting from their action. The high temperature necessary for the curing of bright yellow leaf destroys the enzymes, and this class of tobacco is therefore deficient in aroma. There are three methods of fermentation; the sweating in bulk, the natural sweat after packing in cases, and the forced sweat in case; but the first is generally used, as it can be more easily controlled. The natural sweat of seed-leaf is conducted in large wooden cases, each holding about 300 lbs. of leaf; a space of about half an inch is allowed between the boards, through which the air enters and the moisture escapes. In the autumn the leaves are pressed tightly into the boxes, which are then stored in the warehouse in tiers until the sweat occurring in the following summer is finished. The temperature is maintained fairly uniform, and the loss of weight during the process amounts to from 10 to 14 p.c. White Burley and heavy shipping tobacco are allowed to sweat in bulk for a short time before being prized, or forced into hogsheads by pressure; the hogsheads are large enough to hold from 1200 to 1600 lbs. of tobacco leaf.

Yellow tobaccos are also bulked down for a month or two to fix the colour, and are afterwards packed loosely. Cuba, Sumatra, and other cigar tobaccos are carefully graded according to colour, &c., and are fermented in large bulks varying from 3000 lbs. for the light varieties to 15,000 lbs. for the dark varieties of leaf. The fermentation is allowed to proceed for from 6 to 8 days, and the heaps are then re-made, the outside portions being placed in the centre. The operations are conducted in rooms heated by steam pipes to about 165°F., but if the temperature of the heaps is allowed to rise much above 140°F. the enzymes themselves are liable to undergo oxidation and no good effects result.

Home-grown tobacco. In the year 1886, owing to the agricultural depression in this country, efforts were made to remove the restrictions then existing on the home cultivation of tobacco, and permission was obtained to try experimental growings in several selected localities. These experiments were repeated in the following year, and were sufficiently satisfactory to justify the opinion that tobacco could be grown successfully as a farm crop in the British Isles. Experiments under the auspices of the Department of Agriculture in Dublin were started in Ireland in the year 1900. In the year 1904, the cultivation was commenced on a commercial scale, and in the year 1907 the statutory restrictions were repealed. The Department continues to furnish all possible assistance to the tobacco growers, and from the reports it has published it appears that a total area of about 200 statute acres was devoted to the cultivation of tobacco in the year 1912, as compared with 20 acres in the year 1904. The areas under cultivation were situated in the following counties: King's County, Louth, Meath, Kilkenny, Wexford, Tipperary, and Limerick. The influence of the cool, moist climate favours the production of large thin leaves which are somewhat deficient in gum, resins and aroma; but these defects have to some extent been overcome by prolonging the ripening season, during which the leaf gains in body. Yellow Pryor and selected blue Pryor have so far proved most successful for pipe-tobaccos, and Turkish, Pryor, and hybrid varieties have given the best results for cigarette tobacco. Reasonable hopes are also entertained of producing a satisfactory yellow tobacco. The requisites for success are deep cultivation, a fine soil, and fields protected from cold winds by high hedges or other means. As regards manures, the initial growth is found to be more rapid when farmyard manure is supplemented by artificial manures. The largest yield is obtained on uplands, when manures containing a large proportion of phosphates are used; potash is more effective for moorlands. Nitrogen and phosphates have a tendency to produce a coarse leaf; with potash a smooth leaf is obtained, and the burning qualities are improved, but the growth is somewhat retarded. In consequence of the minute size of the seed, about 300,000 to the ounce, the plant is forced to rely unusually early on external nourishment. The seeds are sown in glass-covered hot-beds some time between the middle of March and the middle of April, and the plants are transplanted at the latest by June 1st. The usual cultural details are followed: insect pests, on the whole, are not so troublesome as they are abroad, but the cool, moist climate greatly increases the tendency to produce suckers. 'Topping' of all the varieties, except Turkish, is usually practised. Ripening is hastened by the 'topping' and 'suckering' operations, but the usual indications, change of colour, curling of the edges of the leaf, &c., are not so manifest under Irish climatic conditions. Harvesting lasts from about the end of July to mid-October, according to whether the leaves are primed off as they ripen, or whether the whole plant is harvested with the leaves still attached to the stem. The practice of allowing the plants to wilt in the open air on scaffolds, which are capable of being protected from heavy rains, has been found very valuable. Air-curing, supplemented by suitable artificial heat at critical periods, has proved to be the best method for most classes of tobacco. The subsequent preparation of the leaf for the market involves the usual operations of grading or sorting, fermentation in bulk, and ageing, after the tobacco is packed. A statute acre of land yields on the average about 1000 lbs. of tobacco at a cost of from £20 to £60.

The enactments against the growth of tobacco in Scotland and England were repealed by the Finance Act of the year 1909–1910.

Provision is now made for the remission of the duty on such home-grown tobacco as is used for the preparation of tobacco extract for insecticidal purposes. An approved denaturant must, however, be added to the extract before it is allowed to pass out of revenue control.

Composition. The tobacco plant contains a large number of substances common to the vegetable kingdom, among which may be mentioned cellulose, starch, albuminoids, glucosides, resins, chlorophyll, and many organic acids. On the character and proportion of these organic substances depend largely the uses to which the several varieties of tobacco are put. The freshly-cut green leaves contain from 80 to 90 p.c. of moisture: the normal percentage in the leaf when ready for the market is about 14 p.c., but in the finer grades of cigar and other leaf 20 p.c. is not uncommonly found. The amount of nicotine, the characteristic constituent of tobacco, varies from about 1 to 10 p.c.: thick-leaved varieties contain more than those with thin leaves, and the top leaves of a plant are richer in nicotine than those at the base of the stem. Schloesing has shown that the amount present in the leaves increases as growth proceeds: from leaves of the same kind collected on May 25, August 27, and September 25, he obtained 0·79, 2·27, and 4·32 p.c. of nicotine respectively. The dark, heavy tobaccos contain considerably more nicotine than the light coloured varieties. The use of large quantities of nitrogenous manures also favours the production of an increased quantity of nicotine. Java leaf contains from 1 to 2 p.c., Havannah, Maryland, Manila and Turkish from 2 to 4 p.c., Virginia and Kentucky up to 7 p.c., while some heavy French varieties contain as much as 10 p.c. of nicotine. The organic acids present in tobacco are chiefly malic, citric, oxalic, and pectic; acetic acid is sometimes found in fermented leaves. Some proportion of these acids exists in combination as acid salts and gives an acid reaction to the cell-sap. The malates, owing to their hygroscopic properties, are said by Behrens to exercise a considerable influence on the 'life' of the leaf by preserving its elasticity and softness. The changes in the colour of the leaf which occur during the curing process are concomitant with considerable chemical changes in the composition, brought about partly by the etiolation of the chlorophyll granules, and the subsequent oxidation of the sap contents of the dead cells. The acidity of the leaf, the soluble albuminoids, and the starch also through the action of the diastase, markedly diminish. Further changes of a complex character occur in the sweating process. The nicotine which exists in the leaf in combination with various organic acids is partially liberated, and part of it and of the amino bodies and albuminoids also, are eliminated. The nitric acid, ammonia, and the starch-content are little affected, but excessive fermentation favours the production of ammonium salts. Many attempts have been made to isolate and identify the bodies which impart the aroma to tobacco, but they have so far proved unsuccessful. At one time the source of the aroma was believed to be the so-called tobacco-camphor, or nicotianin, a crystalline volatile substance obtained by the steam distillation of fermented tobacco; but experiments have shown that it is not always associated with nicotine in tobacco leaf, as was supposed. The theory of Suchsland, that the distinctive aromas which characterise the different types of tobacco are due to the action of specific bacteria during the sweating process, has not been substantiated by other observers. The quality of the aroma is liable to be deteriorated by imperfect curing or a high fat content in the leaf. The formation of the aromatic bodies, however, is believed to be closely connected with the considerable reduction in the nicotine-content of the leaf which takes place during the fermentation process. It is a well-known fact that a high nicotine-content in a cigar is often associated with a poor aroma. The aromatic matters of tobacco are soluble in water, and more or less so in alcohol, and are readily dissipated by heat. The odour developed in smoking a cigar may be due partly to the mere volatilisation of the aromatic products of the sweating process and partly to the destruction of certain constituents. Nicotine, ammonia, carbon monoxide, pyridine, trimethylamine, butyric acid, and traces of nicotianin, hydrogen cyanide, formaldehyde and hydrogen sulphide, in addition to water and carbon dioxide, have been found in tobacco smoke. Kissling recovered from the smoke of two different samples of burning tobacco, each containing originally 3·75 p.c. of nicotine, 27·8 and 52·0 p.c. of the nicotine, while the quantity in the unconsumed portions of the tobacco increased to 4·5 and 5·9 p.c. respectively.

The following table of the analyses of certain kinds of tobacco serves to show the wide differences in the composition of various typical varieties. It is compiled from the results of analysis of many kinds of tobacco, which were made in the Inland Revenue Laboratory under the direction of Dr. James Bell.

PERCENTAGE COMPOSITION OF TOBACCO DRIED AT 100° C.

Constituents	Manila	Virginia Ripe	Virginia Bright	Turkey	Havana	Latakia	Kentucky	German	Java	China
Nicotine	3·00	3·86	2·20	0·90	3·98	1·17	4·59	3·22	3·30	2·50
Malic acid (anhydride)	10·72	9·06	4·17	4·90	12·11	9·07	11·57	12·94	6·04	7·46
Citric „ „	3·94	3·09	1·00	1·90	2·05	2·40	3·40	2·89	3·30	1·58
Oxalic „ „	3·72	1·58	1·72	1·38	1·53	1·98	2·03	2·51	3·38	3·91
Acetic „ „	0·36	0·80	0·35	0·14	0·42	0·36	0·43	0·34	0·22	0·31
Tannic „ „	0·30	1·34	6·32	3·39	1·13	2·33	1·48	0·68	0·51	3·13
Pectic „ „	10·63	7·72	7·51	9·62	11·36	6·25	8·22	10·23	10·13	7·48
Nitric „ „	0·43	0·43	0·14	0·05	1·32	0·76	1·88	0·37	0·23	—
Cellulose	11·73	10·38	12·64	9·72	15·76	10·00	12·48	14·48	11·82	7·98
Starch	—	—	1·73	6·28	—	0·69	—	—	—	1·54
Saccharine matter	—	—	14·59	12·07	—	1·46	—	—	—	12·93
Ammonia	0·30	0·05	0·03	0·05	0·49	0·10	0·19	0·32	0·23	0·04
Insoluble albuminoids	11·27	14·29	4·68	5·30	9·75	7·25	8·10	6·62	9·53	4·49
Resins and chlorophyll	7·51	5·21	3·41	7·90	5·15	6·62	1·99	2·13	6·45	6·02
Fatty substances	2·04	1·07	2·27	0·49	1·03	1·12	2·28	0·89	0·81	0·25
Soluble extractive matter rich in Nitrogen	8·34	16·24	13·47	13·24	7·74	18·97	13·90	8·10	10·39	14·35
Indefinite insoluble matter	9·45	12·93	12·41	9·71	8·68	14·94	13·10	12·56	15·20	12·61
Mineral matter	16·26	11·95	11·36	12·96	17·50	14·53	14·36	21·72	18·46	13·42

The amount of ash found in tobacco varies greatly, and when calculated on the dry leaf ranges from about 10 p.c. to as much as 25 p.c., or even more. The lowest amount is found in the light varieties used for making cigarettes, and the greatest amount in leaf intended for making cigars. The ash of tobacco invariably contains potash, lime, magnesia, iron-oxide, alumina, soda; carbonic, silicic, sulphuric and phosphoric acids, and chlorine. The potash, which exists in the tobacco mainly in combination with the organic acids, may be present to the extent of fully 30 p.c. of the total amount of the ash. The amount of lime present is generally lower than that of potash: magnesia and silica rank next, while the amounts of soda, alumina and iron-oxide are relatively small. Lithia and manganous oxide are occasionally present in very small quantities. The combined chlorine varies from a mere trace to as much as 15 p.c. of the total amount of the ash.

The table (p. 509) shows the percentage composition of the ash of the several kinds of tobacco enumerated in the preceding table.

The leaves of tobacco contain more magnesia and silicic acid, and less alkali, phosphoric acid and chlorine than the stalks. The nitrates are confined almost entirely to the stalks and stems of the young plant, and decrease in amount as the plant comes to maturity: analyses of cigar-stalks from Missouri and Connecticut showed from 0·5 to 0·75 p.c. of nitrates, as against 0·15 p.c. found in cigarette leaf. Home-grown tobacco contains as a rule a considerably higher percentage of ash than is present in similar varieties grown abroad: this is probably accounted for by the use of excessive or unsuitable manures, especially when large quantities of chlorine are present, as the tobacco plant is very voracious and will take up almost anything from the soil. Good burning qualities in tobacco are associated with a high percentage of ash, rich in lime and potash, in proper combination: chlorine, except in the presence of much potash and lime, has a decidedly retarding effect on the combustion, but silicic, phosphoric and sulphuric acids have not a detrimental effect. Albuminoids hinder, but cellulose

PERCENTAGE COMPOSITION OF ASH.

Constituents	Manila	Virginia Ripe	Virginia Bright	Turkey	Havana	Latakia	Kentucky	German	Java	China
Percentage of ash on dry tobacco (excluding sand)	21·40	14·96	12·32	12·92	21·40	18·18	17·98	25·88	18·80	14·76
Potash	16·25	34·16	22·19	14·51	11·83	19·57	16·78	—	14·06	14·44
Potassium chloride	6·45	2·53	7·01	19·29	12·68	4·06	2·41	24·98	19·61	3·73
Soda	0·54	0·86	1·46	0·54	0·81	0·55	0·06	—	0·67	0·41
Sodium chloride	—	—	—	—	—	—	—	0·60	—	—
Lime	33·26	18·90	21·70	22·54	33·06	34·69	29·51	35·66	22·30	31·09
Calcium chloride	—	—	—	—	—	—	—	5·89	—	—
Alumina	0·22	0·29	0·89	0·76	0·76	0·68	0·19	0·42	1·79	0·97
Iron sesquioxide	0·18	0·40	2·44	0·43	0·45	0·55	0·82	0·23	0·84	1·10
Magnesia	7·22	6·74	12·44	9·21	5·29	5·53	6·78	6·45	8·52	12·70
Silica	1·59	1·55	0·57	2·06	1·07	2·03	4·94	0·86	6·16	3·38
Phosphoric anhydride	3·92	3·23	4·72	6·39	4·17	3·62	3·86	2·19	6·67	5·11
Sulphuric "	4·47	4·32	8·29	5·20	4·34	3·67	5·07	3·47	7·84	4·83
Carbonic "	25·90	27·02	18·29	19·07	25·54	25·05	29·58	19·25	11·54	22·24
Percentage of sand on dry tobacco	0·60	0·95	1·28	1·80	1·80	0·92	5·26	0·94	1·72	2·12

promotes the good burning qualities of tobacco; while nicotine appears to be an unimportant factor. The comparative burning qualities, estimated by the time of glowing of the kindled leaf, vary from about four seconds in yellow varieties to as much as 175 seconds in Pennsylvania cigar-leaf.

Tobacco is analysed as regards organic and inorganic constituents by the usual methods described in text-books dealing with agricultural and quantitative chemical analysis. Special processes applicable to tobacco are described in the report on the culture and curing of tobacco in connection with the 10th United States Census of 1880. The percentage of moisture is liable to be under-estimated if the drying-oven is not maintained at a temperature of 100° and the ash also, unless it is re-carbonated by the addition of strong solution of ammonium carbonate, and subsequently dried before ascertaining the weight. A convenient method for the estimation of nicotine in tobacco is that of Kissling, which is as follows: Take 20 grms. of tobacco, finely powdered and dried at a temperature not exceeding 60°, and grind it up in a mortar with 100 c.c. of alcoholic solution of soda (6 grms. of NaOH dissolved in 40 c.c. of water and then made up to 100 c.c. with absolute alcohol). Transfer the mass to a Soxhlet extraction apparatus and extract for 3 hours with ether. Remove as much of the ether as possible by careful distillation, mix the residue with 50 c.c. of a 4 p.c. solution of soda, and distil in a current of steam. The flask containing the nicotine extract should be connected with the condensing apparatus by means of a tube having a safety bulb, and the distillation conducted rapidly and in such a manner that when 200 c.c. of the distillate have been collected not more than 15 c.c. of liquid remain in the distilling flask. Titrate the distillate with decinormal H_2SO_4, using litmus or lacmoid paper as an indicator. By using a series of test papers and noting the burette-reading against each, the exact point of neutralisation can readily be ascertained when the papers are dry.

Manufacture. In several European countries, among which may be mentioned France, Spain, Italy, Austria-Hungary, and Turkey, the manufacture of tobacco is a State monopoly, and in Spain the cultivation of tobacco is strictly prohibited. In Germany, Holland, and other European countries the manufacture is in private hands. In the United Kingdom, tobacco is subjected to a heavy import duty, and certain legal restrictions are imposed, which, however, chiefly affect the manufacturers of the commoner kinds of tobacco. The only substances allowed to be used in the manufacture are water, acetic acid, essential oils, and olive oil—the latter in the spinning of roll tobacco. The finished article must not contain more than 32 p.c. of moisture, and if it is roll tobacco, not more than 4 p.c. of olive oil. The leaves of plants other than tobacco may not be employed, nor any preservative used except acetic acid. Essential oils for flavouring purposes may be added to snuff, and the addition is allowed of the carbonates, chlorides and sulphates of sodium and potassium, ammonium carbonate, and of 1 p.c. of lime in the form of lime-water. The snuff, when dried, however, must not contain more than 26 p.c. of alkaline salts nor more than 13 p.c. of the oxides of lime and magnesia, inclusive of the amounts naturally present in tobacco. More latitude is allowed in the manufacture of tobacco in bonded factories: the addition of foreign leaves is not permitted, but any suitable sweetening or flavouring matter may be used. Sugar, honey, liquorice, glycerin, gum, salt, and logwood are the ingredients most commonly used for this purpose in the manufacture of this kind of tobacco, which is known as Cake- or Cut-Cavendish, and is manufactured chiefly for exportation. If intended for home consumption, this tobacco is required to be enclosed in a specially designed Customs' wrapper to distinguish it from the ordinary article, and it is subjected to a higher rate of duty. The sale of cigarettes containing sweetening matter is not permitted, and no flavouring materials may be used in cigars.

Tobacco leaf is imported into this country either entire or with a portion of the mid-rib removed, in which case it is called 'strips': as a slightly higher rate of duty is charged on the latter, a much larger proportion of the entire leaf is now imported. Nearly 90 p.c. of the raw material imported comes from America; 5 p.c. comes from the Dutch Indies, and about 1 p.c. is obtained from the British colonies, of which North Borneo produces a large proportion. The principal kinds of tobacco used are Virginia, Kentucky, Western, Burley, Ohio, Perique, Havannah, Japan, Java, China, Sumatra, Borneo, Turkish, Latakia, and German. The more tender varieties, such as Turkish, are packed carefully in bales leaf upon leaf, but hogsheads are the usual packages employed, in which the leaves are packed either in layers or in bunches of ten to a dozen leaves, bound round with another leaf and known as 'hands.' Commercial tobacco is classified as a rule under five heads—common, middling, good, fine, and selected; but each manufacturer has his own particular method of assortment. Price, colour, texture, burning qualities, aroma, and body or drinking power, that is, ability to absorb and retain moisture without becoming too wet, are all factors which influence manufacturers in selecting tobacco.

Imported leaf, although apparently dry, usually contains from 10 to 20 p.c. of moisture, but 14 p.c. may be regarded as a fair average. There are two rates of duty on imported leaf tobacco depending on the amount of moisture present: the duty on leaf containing 10 p.c. or more of moisture is *5d.* per lb. lower than the duty charged on leaf containing less than 10 p.c. of moisture. The manufacturer of the cheaper kinds of tobacco endeavours therefore to secure leaf containing moisture as little in excess of 10 p.c. as possible, and so to obtain a larger profit from the greater amount of water he can add in the process of manufacture. In cigarette, cigar, and other varieties of leaf requiring careful handling, a higher initial percentage of moisture is desirable, and these varieties of leaf sometimes contain as much as 20 p.c. of moisture.

The principal kinds of manufactured tobacco are cut, twist or roll, and cake tobacco; cigars, cigarettes, and snuff. Many kinds of leaf are blended for manufacturing cut tobacco, and in the commoner kinds a considerable quantity of leaf other than American is employed. These other kinds are known as 'substitutes,' and their introduction dates back to the time of the civil war in the United States of North America, which caused a temporary shortage in the supplies of Virginia leaf tobacco. Many of these 'substitutes' have the distinct advantage of being able to retain a large quantity of moisture without appearing to be unduly moist.

The first process in manufacturing tobacco is the 'liquoring' stage: the old crude method of employing a watering-pot has now been superseded by the use of steam appliances which ensure a more even distribution of the moisture. When 'strips' are not employed, the mid-rib of the leaf which absorbs more moisture than the lamina is then removed—this operation is called 'stripping.' A mechanically actuated knife is employed to cut the tobacco into shreds: 'shags' and such like tobaccos undergo the further process of 'panning,' which consists in thoroughly mixing up the cut tobacco on copper trays heated to a suitable temperature; the tobacco is then set aside to cool on racks. The moisture in the common kinds averages about 30 p.c., but the better kinds of smoking mixtures contain from 15 to 25 p.c. The distinctive flavours of these tobaccos are due either to the presence of Latakia, Perique, &c., in the blend of leaves used or to the addition of essential oils, such as oil of cassia, geranium, cloves, bergamot, and winter-green. Acetic acid is employed as a preservative. For 'twist' tobacco the darker varieties of American leaf, such as Kentucky, Western, Clarksville, &c., are chiefly employed, but a fair quantity of Irish-grown leaf is now used in this class of tobacco. 'Twist' tobacco is made either by hand or on a spinning-wheel: the damp strips or 'fillers' are formed into ropes, the thickness of which depends on the denomination of 'twist' intended to be manufactured, and these ropes are enclosed in a covering wrapper of leaf. The tobacco, at this stage, is known as 'brown twist,' for which a considerable demand exists, chiefly in the North of England. If the tobacco is intended for 'black twist' the rope of tobacco is made up into 'rolls,' consisting of several concentric layers superimposed one on the other. The rolls, after being enclosed in oiled cloths, and tightly bound up with rope, are then baked in steam-heated hydraulic presses until the tobacco assumes a rich black colour, and develops its full aroma; they are then removed to a cold press until cool and fully matured. In order to prevent the coils from sticking to one another in the rolls, olive oil is applied to the tobacco during the 'spinning' and 'rolling' or 'making up' processes, but the amount of oil used is regulated so as to ensure that the finished tobacco does not contain more than 4 p.c. of oil. Acetic acid and essential oils are also employed. Special names are given to different forms of 'twist,' *e.g.* the terms ladies' twist, or Alloa twist, Liverpool roll, pigtail and bogie, have reference to the thickness of the rope; Negrohead indicates a plaited variety; nailrod is in the form of sticks, and target is a thick twist coiled up in a single layer. 'Cake' tobacco is prepared either by pressing 'spun' tobacco or by moulding the damp strips under pressure and then adding an outer covering of leaf. 'Flakes' and 'Cut Cavendish' are obtained by cutting these cakes.

The leaf employed for the manufacture of high-class cigars has to meet many requirements, and blends of different varieties are therefore employed. The component parts of a cigar are the 'filler,' the 'bunch wrapper,' shaped like a balloon gore, and cut from a fairly good strip, and the 'outer wrapper.' The outer wrapper of a cigar should be made from a tough leaf with small veins, of a light and uniform colour and should not possess a pronounced flavour, as it comes in contact with the lips and tongue in smoking; the filler must, however, possess a good aroma, emit an agreeable odour on burning, and have good burning qualities. The finest leaf for cigars comes from Cuba, but Sumatra, North Borneo, Java, &c., supply a considerable quantity of the leaf used for cigar-making in this country. The leaves are moistened with water, opened out carefully, deprived of the midrib, smoothed out and sorted; the perfect leaves are cut in halves and are used as wrappers. The 'filler,' consisting of fragments or cuttings of leaf, or sometimes of cut tobacco, is placed on the 'bunch wrapper,' near one end, and the bunch wrapper is then carefully wound round the filler. Over the 'bunch wrapper' the cigar-maker then winds spirally the 'outer wrapper,' which is a long rectangular strip of leaf; the winding is commenced at the open end and finished off at the pointed, or mouth, end. The cigars are then gauged and cut to the proper length, dried and packed. Great dexterity is necessary in making cigars, especially in manipulating and keeping the cigars to shape, size, and weight, as well as in evenly packing. Uniformity in the commoner kinds is secured by the practice of pressing the cigars in moulds before applying the outer wrapper. The moisture in the finished cigar is reduced to about 10 to 15 p.c. by storage in a drying-room.

The manufacture of cigarettes was introduced into this country by a Greek in the year 1860, and originally Turkish varieties of tobacco only were employed, but now a considerable quantity of bright American leaf is also used. This branch of the tobacco industry is highly specialised, as the character and the aroma of a cigarette depend on the suitable blending of the various kinds of tobacco employed. The tobacco used for cigarettes is comparatively dry, the moisture added is just sufficient to permit of the leaf being satisfactorily cut by the machines. The finer varieties of cigarettes are invariably made by hand, either by rolling up the tobacco in the paper, or by filling it into paper tubes closed at one end. In the latter method, charging cylinders slightly smaller in diameter are used, and the tobacco is transferred therefrom to the tubes by means of a rod; the closed ends of the paper tubes are subsequently cut off. A great impetus has been given to the production of cigarettes by the employment of cigarette-making machines, which can turn out as many as 24,000 cigarettes per hour. The moisture in cigarettes varies according to the time they are stored in the drying-room, but it usually ranges from 12 to 18 p.c.; if the tobacco is made too dry it is liable to be shaken out of the wrapper; and on the other hand, if the tobacco is left too damp, the cigarette will not burn well. Mouthpieces are often fitted to cigarettes made from Turkish tobacco, on account of its superior burning quality. Cigarettes vary considerably in weight; an ounce may contain from 12 to 40 cigarettes, but 20 to 30 is about the average. Sweetening matter is not allowed to be used in making cigarettes, but the paper wrappers of the 'pectoral' kinds sometimes contain a small quantity of saccharin.

Snuff is sold in two forms, dry and moist, the former is made from the stalk or midrib of the leaf, but the latter contains a variable proportion of the lamina. The difference in the quality is dependent on the flavour, the pungency, and the scent. The dry varieties—the Welsh, Scotch, High Toast, and Irish kinds—are, as a rule, more finely ground than the moist varieties. The moisture ranges from about 20 p.c. in Scotch snuffs, to as little as 5 p.c. in Irish snuff. 'Rappees' include such well-known varieties as Latakia, Macuba, and Prince's mixture, and contain from 30 to 50 p.c. of moisture. The tobacco stalks used for snuff-making are cut into small pieces, moistened with water or sometimes with lime-water, and allowed to ferment, the fermentation period frequently lasting for several months. The material, in the case of Scotch snuff, is then ground to the required degree of fineness, dried down, flavoured, and sifted. The stalks for Irish and Welsh snuff, before being ground, are gently roasted, by which means the characteristic odour of these varieties is produced. For moist snuffs the material is ground wet in a special kind of mortar, and is then allowed to ferment until the required depth of colour is produced. Certain kinds of alkaline salts are mixed with the snuff-flour to increase its pungency, but, as already mentioned, the quantity and the kinds which may be employed are defined by statute. Essential oils, ground orris-root and ground Tonquin beans are used for flavouring purposes. Adulteration of snuff is now rarely practised, but such substances as the oxides of iron, red lead, lead chromates, &c., have been used as colouring materials, and chalk, magnesia, borax, sand, and excessive quantities of alkaline salts have been employed to increase the weight.

Prior to the passing of the Pure Tobacco Act of the year 1842, the adulteration of tobacco with sugar, treacle, honey, gum, &c., and such foreign vegetable matters as rhubarb, coltsfoot, &c., was very general; but in consequence of the heavy penalties imposed by that Act and the vigilance of the Revenue Authorities these practices have almost ceased. The enactments relating to the amounts of moisture and oil in tobacco are also strictly enforced. Such substances as malt combings, moss-litter, &c., are occasionally offered as substitutes for tobacco, but the offenders rarely escape detection and punishment. Manufactured tobacco contains frequently considerable quantities of sand, and manufacturers are sometimes suspected of using it as an adulterant. The leaf, however, frequently comes into their possession still retaining a large proportion of the sand which is deposited upon it from the soil by the action of the wind and rain during growth. A portion of this sand only is detached from the leaf during the manufacturing operations, which accounts for the presence of sand in the finished article.

In the manufacture of tobacco, a considerable quantity of waste material is produced, siftings, sweepings, &c., and in addition the quantity of stalks obtained by stripping the midrib from the imported leaf is far in excess of that required for conversion into commercial snuff. Repayment of the duty, called 'drawback,' is made by the Revenue Authorities on this refuse of tobacco when it is deposited in an approved warehouse to be abandoned to the Crown, or in a bonded factory to be utilised in the manufacture of nicotine or the preparation of 'sheep-dip,' hop-powder, insecticides, &c.

Statistics. The amount of tobacco leaf imported into the United Kingdom and the consumption of manufactured tobacco have steadily increased. The imports in the year 1851 amounted to about 28,000,000 lbs. and the consumption was just over 1 lb. per head of the population; in the year 1911, the amount imported was nearly 91,500,000 lbs. and the consumption was slightly in excess of 2 lbs. per head of the population. The manufacture of tobacco is now one of the most important of the minor industries, and according to the returns made in connection with the recent Census of Production, the number of persons employed in tobacco factories in the year 1907 was 37,456. The net value of the raw material was £17,988,000 and, including 11,816,000 lbs. of manufactured tobacco exported, the output amounted to 108,292,000 lbs., representing a money value of £23,799,000. The weight of the different kinds was as follows: of cut and roll tobacco, 69,880,000 lbs.; of cigarettes, 29,904,000 lbs.; of cigars, 3,696,000 lbs.; of sweetened cavendish, 3,136,000 lbs.; and of snuff, 1,568,000 lbs. The degree of the popularity of the principal kinds of tobacco may be ascertained from these figures; the percentages are: of pipe tobacco 67·5 p.c., of cigarettes 29·0 p.c., and of cigars 3·5 p.c. respectively.

Tobacco occupies an important position as a source of revenue in the fiscal systems of most civilised countries. In the tariff of the United Kingdom the rate of duty at the present time is 3*s.* 8*d.* per lb. for normal leaf tobacco, and the net amount of duty paid into the Exchequer in the financial year 1911-12 exceeded seventeen and a quarter million pounds sterling.

D. A. G.

TOBACCO-SEED OIL. Tobacco seeds yield on pressing about 30 p.c. of a greenish-yellow, mild, and odourless oil, sp.gr. 0·923 at 15°, solidifying at −25°, which quickly dries when exposed to the air.

TODDALIA ACULEATA (Pers.). This Indian plant, belonging to the *Rutaceae*, is a rambling shrub found in the sub-tropical Himalayas, in the Khasia mountains, and throughout the Western Peninsula and Ceylon.

The root bark is used in Madras as a yellow dyestuff, and it is also highly spoken of by various writers as one of the most valuable Indian medical products, possessing tonic, stimulant, and antipyretic properties. It was introduced into European medicine in 1771, and at one time enjoyed some celebrity under the name of 'Lopez Root,' but it has long since fallen into disuse.

The colouring matter it contains is berberine (Perkin and Hummel, Chem. Soc. Trans. 67, 413).

A. G. P.

TOLENE *v. Tolu*, art. BALSAMS.

TOLIDENE (*Orthotolidene*) *v.* DIPHENYL.

TOLU *v.* BALSAMS.

TOLUENE. *Toluol, Methylbenzene* C_7H_8 or $C_6H_5{\cdot}CH_3$. First discovered by Pelletier and Walter in 1837 (Ann. Chim. Phys. [ii.] 67, 278) among the by-products in the manufacture of illuminating gas from the resin of *Pinus maritima*, and named by them *retinaphtha*. Mansfield found it in coal-tar, Cahours and Völkel in wood-spirit and wood-tar, and De la Rue and H. Müller in Rangoon tar. It is also found in American light petroleum (Young, Chem. Soc. Trans. 1898, 906); in the products of distillation of a large number of substances (Ritthausen, J. pr. Chem. 1854, 61, 74; Bunte, J. Gasbeleucht, 1892, 35, 571, amongst others) and in a number of naturally occurring substances (Poni, Chem. Zentr. 1901, i. 61, and others). Fittig and Tollens prepared it by the action of sodium on a mixture of bromobenzene and methyl iodide in ethereal solution, and thus proved that it was methylbenzene.

It may also be prepared by the action of methyl chloride on benzene in presence of aluminium chloride (Friedel and Crafts, Ann. Chim. Phys. 1884, [vi.] 1, 459) and by other methods (Gardeur, Chem. Zentr. 1898, i. 438; Fromm and Achert, Ber. 1903, 36, 534; Werner and Zilkens, *ibid.* 2116; Mai, *ibid.* 1902, 35, 162; and many others).

The toluene of commerce is obtained from coal-tar by rectification of the fraction boiling between 100° and 120° (Coupier, Dingl. poly. J. 1866, 181, 386; Leuckart, J. pr. Chem. 1890, [ii.] 41, 301).

Toluene may be purified by treatment with sulphuric acid (Friswell, Chem. News, 1893, 68, 27); it may be freed from thiotoluene by treatment with aluminium chloride (Fr. Pat. 240111, 1894; D. R. P. 79505). It is said to be obtained absolutely pure by converting it into the well crystallised potassium toluene-*p*-sulphonate which is subsequently decomposed (Miller, Chem. Soc. Trans. 1892, 1025; *see* also Kelbe, Ber. 1886, 19, 93; Kraemer and Böttcher, *ibid.* 1887, 20, 601).

Properties. Toluene is a colourless liquid, b.p. 111°, m.p. −97° to −99° (Archibald and McIntosh, J. Amer. Chem. Soc. 1904, 26, 305), sp.gr. 0·8812 at 4°/4°; 0·8723 at 15°/15°; 0·8649 at 25°/25°; 0·8237 at 100°/100°. In its solvent powers it closely resembles benzene.

Oxidising agents, such as chromic acid or dilute nitric acid, convert it into benzoic acid; but by treatment, first with chromyl chloride and afterwards with water, it yields benzaldehyde. Similar products are obtained when it is oxidised electrolytically in alcoholic solution and in the presence of sulphuric acid (Puls, Chem. Zeit. 1901, 25, 263). When the vapour of toluene is passed through a red-hot tube, benzene, anthracene, phenanthrene, dibenzyl, and other hydrocarbons are formed (Berthelot, Bull. Soc. chim. 7, 218; Graebe, Ber. 1874, 7, 48). By passing a mixture of the vapours of toluene and benzene through a red-hot tube, Carnelley obtained a highly complex mixture of hydrocarbons (Chem. Soc. Trans. 1880, 702).

Treated with litharge at a dull red heat, it forms stilbene, diphenyl anthracene, and a liquid hydrocarbon. At 335° only the methyl group is oxidised (Vincent, Compt. rend. 1890, 110, 907); the rate at which the side chain is oxidised depends on the nature and position of substituted groups in the nucleus (Cohen and Miller, Chem. Soc. Trans. 1904, 174; Cohen and Hodsman, *ibid.* 1907, 970).

When air charged with toluene vapour is passed over finely divided platinum or manganese dioxide, the temperature rises until the metals become incandescent and the toluene is completely oxidised to carbon dioxide and water. In the presence of iron, nickel or copper oxides, at temperatures between 150°–300°, it is converted to benzaldehyde, but with carbon at 370°, benzoic acid is formed (Woog, Compt. rend. 1907, 145, 124). Substitution may take place either in the nucleus or in the methyl group of toluene. In the former case a mixture of *p*- and *o*- compounds is chiefly formed.

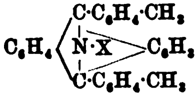
Toluene is employed in the manufacture of nitrotoluene and toluidine, benzyl chloride, benzal chloride, and benzotrichloride, benzaldehyde, benzoic acid, and cinnamic acid. It is also used in the manufacture of dyestuffs, synthetic drugs and perfumes. Formerly toluene formed an essential ingredient of the benzene employed as the starting-point in the manufacture of fuchsin, but at the present day it is usual to start with pure benzene and pure toluene.

Commercial toluene should give only a pale-brown coloration with concentrated sulphuric acid. But pure toluene should give no coloration with sulphuric acid and should not decolorise a N/10 solution of bromine. When shaken with nitric acid (sp.gr. 1·44), the acid should be coloured red but not become viscid or greenish. On distillation a crude toluene should furnish at least 90 p.c. under 120°; and the 'pure toluene' of commerce should distil between 110°–113°—the greater part between 111°–112° (Schultz, Chem. des Steinkohlentheers).

Unless coal-tar toluene has been purified by shaking it with concentrated sulphuric acid, it always contains 2- and 3-methylthiophens (thiotolens).

Toluene reacts with acetylene tetrabromide, methylene chloride or chloroform in presence of aluminium chloride, forming, when the products are well stirred during the reaction, 1 : 6- and 2 : 7-dimethyl anthracenes, m.p. 244·5° and 240° respectively, together with a little β-methylanthracene, benzene, xylene and other homologues (Lavaux, Compt. rend. 1905, 141, 204; *ibid.* 1908, 146, 345).

Like benzene and dimethylaniline, toluene reacts with tetramethyldiaminodiphenylhydroxyanthranol forming a colourless additive compound which yields highly coloured salts and reacts with one molecule of phenylhydrazine or hydroxylamine eliminating two molecules of water and forming the compound



(where X=OH or C_6H_5NH) (Haller and Guyot, Compt. rend. 1903, 137, 606).

Toluene reacts with ethyl diazoacetate at 118° forming ethyl 4-methylnorcaradienecarboxylate, b.p. 122°–126°/15 mm. pressure (Buchner and Feldmann, Ber. 1903, 36, 3509).

Toluene also condenses with benzaldehyde in presence of concentrated sulphuric acid forming di-tolylmethane (Kliegl, Ber. 1905, 38, 84).

Toluene condenses with diphenic anhydride forming fluorene derivates (Pick, Monatsh. 1904, 25, 979).

HALOGEN DERIVATIVES OF TOLUENE.

In the chlorination or bromination of toluene, substitution may, as already mentioned, take place either in the nucleus or in the methyl group. The former is the case when the halogen acts on toluene in presence of iodine or other substances capable of acting as carriers of halogen; the latter, when the halogen alone acts on toluene heated to boiling or exposed to direct sunlight, the influence of light being greater than that of heat in inducing substitution in the side-chain (Cohen, Dawson, Blockley and Woodmansey, Chem. Soc. Trans. 1910, 1623; Bancroft, J. Phys. Chem. 1908, 12, 240). Only the chlorine derivatives belonging to the latter class are of technical importance. Unlike other halogen carriers, sulphur is said to facilitate side-chain substitution (Beck, Ber. 1892, 25, 2445). The latter is also facilitated by the dilution of the halogen (*see* also Cohen and Dakin, Chem. Soc. Trans. 1906, 1455; Holleman and Polak, Rec. trav. chim. 1908, 27, 435).

Benzyl chloride $C_6H_5{\cdot}CH_2Cl$. First obtained by Cannizzaro by the action of hydrochloric acid on benzyl alcohol $C_6H_5{\cdot}CH_2{\cdot}OH$. Manufactured by passing chlorine into toluene contained in acid-proof earthenware vessels and heated to boiling by means of a leaden steam-spiral. The operation is interrupted when the toluene shows the theoretical increase of weight (37·5 p.c.). The vapours are condensed by a reflux worm, and the escaping hydrogen chloride passed into water. The product is shaken with weak alkali and then rectified, by which means it is freed from unaltered toluene and higher chlorinated products. Very good yields are also said to be obtained by allowing sulphuryl chloride to act on excess of toluene in the dark at a temperature a little below 130° (D. R. P. 139552).

For certain other laboratory methods of preparation see Grassi-Cristaldi and Maselli Gazz. chim. ital. [ii.] 28, 498; Solonina, Chem. Zentr. 1898, ii. 887; Schramm, Ber. 1885, 18, 608).

Benzyl chloride is a colourless liquid boiling at 176°–179°; m.p. −43·2° to −48° (Haase, Ber. 1893, 26, 1053); sp.gr. 1·1135 at 4°/4°, 1·1040 at 15°/15°, 1·0967 at 25°/25° (Perkin). Has a somewhat pungent smell; the vapour is very irritating to the eyes. Insoluble in water, but by heating with water to 100°–110°, or by boiling with water for 24 hours with a reflux condenser, it is converted into benzyl alcohol (Niederist, Annalen, 1879, 196, 353); and the same transformation is still more readily effected by boiling benzyl chloride with the calculated quantity of potassium carbonate dissolved in from 8 to 10 parts of water (Meunier, Bull. Soc. chim [ii.] 38, 159; *see* also Vandevelde, Chem. Zentr. 1898, i. 438; Busch and Weiss, Ber. 1900, 33, 2702). Oxidising agents convert it first into benzaldehyde, afterwards into benzoic acid. When subjected to an electric current, hydrochloric acid is evolved and stilbene is formed (Loeb, Zeitsch. Elektrochem. 1903, 9, 903). By heating with a small quantity of copper it yields dibenzyl $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$. With alcoholic ammonia it gives a mixture of benzylamine $C_6H_5{\cdot}CH_2{\cdot}NH_2$, dibenzylamine

$$(C_6H_5{\cdot}CH_2)_2NH,$$

and tribenzylamine $(C_6H_5{\cdot}CH_2)_3N$ (Cannizzaro, Annalen, 1865, 134, 128; *ibid.* Suppl. 4, 24, 80; Dhommée, Compt. rend. 1901, 133, 636). With aniline it forms benzylaniline

$$C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}C_6H_5.$$

When treated with a metallic salicylate at 130°–140° it yields *benzyl salicylate*, an odourless liquid, b.p. 208°/26 mm., which is said to be useful for external application in medicine (Eng. Pat. of 25735, 1899).

Benzyl chloride is used in the preparation of benzaldehyde and benzoic acid, and also for introducing the benzyl group into basic colouring matters so as to produce varieties of shade.

Commercial benzyl chloride generally contains moisture, benzal chloride ($C_6H_5{\cdot}CHCl_2$), benzotrichloride ($C_6H_5{\cdot}CCl_3$), chlortoluenes, and even unchanged toluene. It should show the correct boiling-point and specific gravity. In order to ascertain whether the whole of the chlorine is contained in the methyl group, a weighed quantity of the substance should be boiled for some minutes with a hot saturated alcoholic solution of silver nitrate, using a reflux condenser; the silver chloride, which will represent only the chlorine from the side-chain, is then collected and weighed (Schulze, Ber. 1884, 17, 1675). Benzotrichloride may be detected by the green colouring-matter (malachite green) which is formed when the substance is heated with dimethylaniline and zinc chloride (Döbner).

Benzal chloride. *Benzylidene chloride*

$$C_6H_5{\cdot}CHCl_2.$$

First obtained by Cahours (Ann. Chim. Phys. 1848, [iii.] 23, 329) by the action of phosphorus pentachloride on benzaldehyde $C_6H_5{\cdot}CHO$. Manufactured by chlorinating boiling toluene in direct sunlight.

Colourless, powerfully refractive liquid, boiling at 206°; m.p. −16·1°; sp.gr. 1·2557 at 14°. Water, alkalis, or concentrated sulphuric acid, convert it into benzaldehyde. When heated with sodium acetate it yields cinnamic acid.

Benzal chloride is employed in the manufacture of benzaldehyde, benzoic acid, and cinnamic acid.

The commercial product is always impure. It may be tested by its boiling-point, and by determining the percentage of chlorine.

Benzotrichloride. *Phenylchloroform*

$$C_6H_5{\cdot}CCl_3.$$

First obtained by Schischkoff and Rösing (Compt. rend. 1858, 46, 367) by the action of phosphorus pentachloride on benzoyl chloride $C_6H_5{\cdot}COCl$. Manufactured by chlorinating boiling toluene in direct sunlight until the weight of the product no longer increases.

Colourless, powerfully refractive liquid, boiling at 213°–214°; m.p. −21·2°; sp.gr. 1·380 at 14°. Heated with water at 150°, it yields benzoic and hydrochloric acids. Sodium ethoxide converts it into ethyl orthobenzoate $C_6H_5{\cdot}C(OC_2H_5)_3$. Heated with dimethylaniline and zinc chloride, it yields malachite green. Methyldiphenylamine, diethylaniline, and diamylaniline give similar green colouring matters, differing in shade from malachite green.

Benzotrichloride was formerly employed in the manufacture of malachite green, but owing to the difficulty of obtaining benzotrichloride in a state of purity this process has been abandoned.

Commercial benzotrichloride is tested by examining its boiling-point. It generally contains compounds chlorinated in the nucleus.

Fluorine derivatives of toluene have been obtained by the action of antimony fluoride on benzotrichloride (Swarts, Chem. Zentr. 1898, ii. 26; Holleman, Rec. trav. chim. 1906, ii. 25, 330).

Literature regarding other halogen toluenes and their nitro and other derivatives (Jackson and Smith, Amer. Chem. J. 1904, 32, 168; Hilpert, *ibid.* 1908, 40, 150; Blanksma, Rec. trav. chim. 1904, 23, 125; Chem. Weekblad. 1909, 6, 728; Reverdin, Bull. Soc. Chim. 1904, [iii.] 31, 63; Mascarelli, Atti. R. Accad. Lincei, 1905, [v.] 14, ii. 199; Artmann, Monatsh. 1905, 26, 1091; Zincke and Buff, Annalen, 1908, 361, 218; Willgerodt and Simonis, Ber. 1906, 269; Caldwell and Werner, Chem. Soc. Trans. 1907, 248; Ponzio and Charrier, Atti. R. Accad. Sci. Torino, 1908, 43, 475; Ponzio, Gazz. chim. ital. 1908, 38, ii. 417; Zincke and Frohneberg, Ber. 1910, 43, 857). Cyano toluenes, *see* Borsche and Böcker, Ber. 1903, 36, 4357.

Nitro derivatives; for preparation *v.* **BENZENE AND ITS HOMOLOGUES.**

When toluene is nitrated with nitric acid of sp.gr. 1·475, the quantity of *o-*, *m-* or *p-* mononitro derivative obtained depends on the temperature, solvent and other conditions (Holleman, Proc. K. Akad. Wetensch. Amsterdam, 1908, 11, 248; Bruner and Vorbrodt, Chem. Zentr. 1909, i. 1807; *v.* also Kohn, Monatsh. 1910, 31, 745; Fischer, Zeitsch. Elektrochem. 1910, 16, 161). The first increases slightly with a rise in temperature; the last decreases, whilst the *m-* product also increases, but is always present only in small quantity.

When freshly distilled *o*-nitrotoluene is rapidly cooled to −20° it solidifies sometimes to the labile *α*-modification, m.p. −10·56°, sometimes to the stable *β*-modification, m.p. −4·14°. The latter may also be prepared by cooling the liquid to −50° or −60° when the *α* form separates at first but rapidly changes to the *β* form. Superheating of the vapour during distillation also favours the formation of the latter modification (Ostromisslensky, Zeitsch. Physikal. Chem. 1907, 57, 341).

o-Nitrotoluene reduced by heating with iron or zinc and sodium hydroxide at 100°, yields *o-azoxytoluene*; when, however, acid is added to the product, toluene-*o*-azobenzoic acid separates as orange-red needles with a blue lustre, m.p. 148°, which is reduced by zinc dust and soda to toluene-*o*-hydrazobenzoic acid, m.p. 136°. This when warmed with concentrated hydrochloric acid yields, on addition of sodium hydroxide, diaminomethyldiphenylcarboxylic acid

$$NH_2{\cdot}C_6H_3(CH_3)C_6H_3(NH_2)CO_2H$$

m.p. 183° (decomp.) D. R. P. 145063; *cf.* Löb and Schmitt, Zeitsch. Elektrochem. 1904, 10, 756).

m- and *p*-Nitrotoluenes mixed with carbon tetrachloride react with chromyl dichloride in the same solvent, yielding the corresponding nitrobenzaldehyde and a small quantity of nitrobenzoic acid. The *o*-nitro compound, similarly treated, yields a mixture of chlorinated nitro compounds, the vapours of which attack the eyes severely. The three chlorotoluenes, when similarly treated, yield the corresponding adehydes (Law and Perkin, Chem. Soc. Trans. 1908, 1635).

p- and *o*-Nitrotoluenes and their derivatives, when treated with potash, yield red nitroso dibenzyl and blue nitroso stilbene compounds (Davies and Horsfall, Chem. Soc. Trans. 1907, 2070; Green and Baddiley, *ibid.* 1908, 1721. Ring substituted *p*-nitrotoluenes are converted by an alcoholic solution of sodium disulphide into the corresponding *p*-aminobenzaldehydes and *p*-toluidines (Blanksma, Chem. Weekblad, 1909, 6, 899).

For other information on the nitrotoluenes and some of their derivatives, *v.* Cohen and Dakin, Chem. Soc. Proc. 1901, 214; Glasmann, Ber. 1903, 36, 4260; Bamberger and Hübner, *ibid.* 3803, 3822; South, Bull. Soc. Chim. 1904, [iii.] 31, 133; Cohen and Marshall, Chem. Soc. Trans. 1904, 527; Walker and Spencer, *ibid.* 1108; Siegfried, Zeitsch. Physiol. Chem. 1904, 43, 68; Zincke, Annalen, 1905, 339, 218; Raikow and Urkewitsch, Chem. Zeit. 1906, 30, 295; Brand and Zöller, Ber. 1907, 40, 3324; Reissert, *ibid.* 4209; Hofer and Jakob, *ibid.* 1908, 41, 3187; Reverdin, *ibid.* 1909, 42, 1523; D. R. PP. 150313, 182217, 182218.

Amino toluenes, see TOLUIDINE.

Sulphonic derivatives of toluene are obtained by treating toluene with sulphuric acid. If the fuming acid is used and the temperature of the reaction is kept at the boiling-point of toluene, the main product is the *p*- acid, but if the temperature is not allowed to rise above 100° and ordinary concentrated acid is employed, 40–50 p.c. of the *o*- sulphonic acid is obtained (D. R. P. 35211, 137935; Eng. Pat. 10810, 1897; Norton and Otten, Amer. Chem. J. 1888, 10, 140; Bourgeois, Chem. Zentr. 1900, i. 253; Reverdin, Ber. 1909, 42, 1523).

They may be separated from one another by taking advantage of the difference in solubility of the potassium salts, or by conversion into their corresponding sulpho-chlorides or sulphonamides (*v.* SACCHARIN).

The *o*- acid crystallises in octahedra whilst the *p*- acid is obtained as a syrup which condenses with tetramethyldiaminobenzhydrol in the presence of sulphuric acid, forming the leuco base of a sulpho acid of the malachite green series which on oxidation gives a bluish-green dye (D. R. P. 87176). Both acids give metallic and other salts.

o-Toluene sulphonyl chloride may be obtained by treating the corresponding sulphonic acid with chlorosulphonic acid. After standing for several hours the mixture is poured into ice-cold water (Eng. Pat. 2304 of 1905; D. R. P. 154493; *see* also Eng. Pat. 6581 of 1897; 4525 of 1900; 11077, 11078 of 1898; 16299 of 1903; Fr. Pat. 312797 of 1901).

The *o*- and *p*-sulphonic chlorides may also be prepared conveniently by treating toluene with fuming sulphuric acid containing about 60 p.c. of the anhydride and previously saturated with dry hydrogen chloride (Eng. Pat. 1877 of 1903).

2 : 6-*Di*- and 2 : 3 : 6-*tri-chlorotoluene* 4-*sulphonyl chlorides* have been prepared by treating *p*-toluenesulphonyl chloride with antimony pentachloride at 70°–75°, then treating the mass with alkali and separating the chlorides by fractional distillation (D. R. P. 210856).

For other derivatives of toluene sulphonic compounds, *see* Chattaway, Chem. Soc. Trans. 1904, 1184; Reverdin and Dresel, Ber. 1904, 37, 4452; Willstätter and Pfannenstiehl, *ibid.* 1905, 38, 2244; Ullmann and Nádai, *ibid.* 1908, 41, 1870; Hilditch and Smiles, *ibid.* 4113; Ullmann and Werner, Annalen, 1903, 327, 120; D. R. P. 150366, 146946; Fr. Pat. 328170 of 1902; Morgan and Pickard, Chem. Soc. Trans. 1910, 56.

2-*Amino*-p-*tolyltoluene*-p-*sulphonate*

$$C_7H_7{\cdot}SO_2{\cdot}O{\cdot}C_7H_6{\cdot}NH_2$$

lustrous prisms, m.p. 78°, is obtained by reducing the corresponding nitro compound. It is employed in the manufacture of colouring matters (D. R. P. 201377).

Stable violet-blue dyes have also been obtained from p-*toluenesulphon*-p-*nitroanilide* (D. R. P. 224499).

p-*Toluene sulphinic acid*, m.p. 86°–87°, may be obtained by the action of sulphur dioxide and aluminium chloride on toluene or its halogen derivatives at low temperature (Knoevenagel and Kenner, Ber. 1908, 41, 3315; Thomas, Chem. Soc. Trans. 1909, 342). Its anhydride has m.p. 75° (Knoevenagel and Polack, Ber. 1908, 41, 3323).

Phenols or naphthols when heated with benzene and *p*-toluene sulphinic acid to 150°–180° yield dyestuffs which are readily reduced and are soluble in alkalis (Heiduschka, J. pr. Chem. 1910, 81, 320).

Mercury (Peters, Ber. 1905, 38, 2567), sodium (Gutmann, *ibid.* 1909, 42, 480) and other derivatives of toluene sulphinic acid have been described (Kohler and Reimer, Amer. Chem. J. 1904, 31, 163).

Potassium 4-xantho-2-nitrotoluene-5-sulphonate, $C_{10}H_{10}O_6NS_3K,1\frac{1}{2}H_2O$, forms small light brown prismatic needles, decomposing above 150°. When hydrolysed with potash, it yields dipotassium 6-nitro-4-thiotoluene-3-sulphonic acid, $C_7H_5O_5NS_2K_2,2H_2O$, dark red prisms, oxidised by atmospheric oxygen to the disulphide $S_2[C_6H_2Me(NO_2)SO_3K]_2,5H_2O$, long yellow needles yielding with phosphorus pentachloride the sulphochloride

$$S_2[C_6H_2Me(NO_2)SO_2Cl]_2$$

as light brown prisms, m.p. 208°. The last, on reduction is converted into 2-*amino*-4 : 5-*dithiotoluene* which gives well-characterised salts and esters and is oxidised by air with formation of a substance $(C_7H_7NS_2)_x$. The amino dithiotoluene derivative yields red azo wool dyes (Fichter, Fröhlich and Jalon, Ber. 1907, 40, 4420).

p-*Tolyl-α-naphthylamine* is used industrially in the manufacture of 'Night Blue.' The monosulphonic acid of *p*-tolyl-*α*-naphthylamine is prepared by treating the acetyl compound with sulphuric acid monohydrate. When treated with nitrous acid it yields the corresponding *nitrosamine*, golden yellow needles, m.p. 102°, which is converted by alcoholic hydrochloric acid into p-*tolyl*-4-*nitroso-α-naphthylamine*, crimson needles, m.p. 161°, reacting with *p*-nitrobenzoyl cyanide to form p-*tolylamino-α-naphthyl*-4-*cyanoazomethine*-p-*nitrophenyl*, lustrous violet scales, m.p. 218°.

A tolylated *Nile Blue* (tolylaminonaphthodimethylaminophenoxazonium chloride) is obtained by warming *p*-tolyl-*α*-naphthylamine with nitrosodimethyl-*m*-aminophenol in glacial acetic acid, or by heating Meldola's Blue with *p*-toluidine. If nitrosodiethyl-*m*-aminophenol is used, an analogous dyestuff—*Ethyl Nile Blue*—is formed (Gnehm & Rübel, J. pr. Chem. 1901, [ii.] 64, 497).

Tolyl sulphocarbazole, pale yellow needles, m.p. 127°–128°, is prepared from potassium carbazole and *p*-toluene sulphonyl chloride. It combines with *p*-nitrosophenol, yielding a dark blue powder which on reduction forms a greyish-white leuco compound (D. R. P. 224951).

m-*Tolylenediamine-carbamide* prepared by passing phosgene gas into a solution of *m*-tolylene-diamine and sodium acetate, is a white crystalline powder, m.p. above 300°, insoluble in ordinary solvents (D. R. P. 146914).

Tolylene dicarbamide when fused with sulphur at 200°–230° yields an orange dye (D. R. P. 153916).

m-*Tolyl semicarbazide* (*maretin*) may be obtained by treating *m*-tolyl hydrazine with cyanic acid or its salts or with urea, carbamic chloride or urethanes and by other methods (U. S. Pat. 765164, 1904; Eng. Pat. 7954, 12440, 18825, 1904; Fr. Pat. 349968, 1904; D. R. P. 157572; 160471, 162630, 163035, 163036). It forms colourless crystals, m.p. 183°–184°, soluble in hot water and alcohol and is said to possess antipyretic properties.

For *tolylcarbinol* and some of its derivatives *v.* Tiffeneau & Delange, Compt. rend. 1903, 137, 573; Fournier, *ibid.* 716; Perkin & Pickles, Chem. Soc. Trans. 1905, 652; D. R. P. 154658.

p-*Tolyl arsonic acid* $MeC_6H_4{\cdot}AsO(OH)_2$ is prepared by passing a rapid stream of chlorine through aqueous *p*-tolyl arsenious chloride $C_7H_7AsCl_2$ (Martindale, J. Soc. Chem. Ind. 1909, 910). The tolyl radicle enters into the composition of a large number of other substances (*v.* AZINES and AZO- COMPOUNDS).

Toluic acids are formed by oxidation of the corresponding xylenes with dilute nitric acid and also by other methods (D. R. P. 79028; Scholl and Nörr, Ber. 1900, 33, 1055).

The *o*-acid has m.p. 103·5°–104° and condenses with tertiary aromatic amines forming dyestuffs of the malachite green series (D. R. P. 101426).

The *p*-acid has m.p. 180°, b.p. 264°, and condenses with tetramethyldiaminobenzhydrol forming a triphenylmethane dyestuff (D. R. P. 90881). The *m*-acid has m.p. 108°–109°.

When sulphur monochloride reacts with silver *o*-, *m*-, or *p*-toluate, the *o*-, *m*-, or *p*-compound $(C_6H_4Me{\cdot}CO_2S)_2$ is formed. These compounds decompose gradually on standing and more quickly when heated, forming sulphur, sulphur dioxide, and the corresponding toluic anhydride (Denham, Chem. Soc. Trans. 1909, 1239).

For other information on the toluic acids and their derivatives see: J. Soc. Chem. Ind. 1895, 800; Labhardt, Zeitsch. Elektrochem. 1902, 8, 93; Fischer and Wolffenstein, Ber. 1904, 37, 3215; Langguth, *ibid.* 1905, 35, 2062; Jürgens, *ibid.* 1907, 40, 4409; Müller, *ibid.* 1909, 42, 423; Errera and Maltese, Gazz. chim. ital. 1905, 35, ii. 370; Puxeddu and Maccioni, *ibid.* 1907, 37, i. 68; Anschütz, Annalen, 1906, 346, 341, 349, 354; Freundler and Sevestre, Compt. rend. 1908, 147, 981; Sudborough and Roberts, Chem. Soc. Trans. 1904, 241; Crossley, *ibid.* 281; Kay and Perkin, *ibid.* 1905, 1071; Perkin and Tattersall, *ibid.* 1090; Robertson, *ibid.* 1908, 789; Cohen and Dudley, *ibid.* 1910, 1749; Baudisch and Perkin, *ibid.* 1909, 1870, 1883; Meldrum and Perkin, *ibid.* 1889; Bogert and Kropff, J. Amer. Chem. Soc. 1909, 31, 841; Wheeler and Hoffmann, Amer. Chem. J. 1910, 44, 113).

ψ-*m-Toluic acid* (Δ^{a} *δ-Heptadi-inene-δ-carboxylic acid*) $(C{:}HC{\cdot}CH_2)_2{\cdot}CH{\cdot}CO_2H$, m.p. 47°, is readily soluble in most organic solvents, but sparingly soluble in water. When boiled with water or acid it is readily converted to *m*-toluic acid. With ammoniacal cuprous chloride, it yields the yellow copper derivative (Perkin and Simonsen, Chem. Soc. Trans. 1907, 840).

Tolualdehydes or *toluic aldehydes* may be prepared by the oxidation of the corresponding xylenes or their derivatives (Moritz and Wolffenstein, Ber. 1899, 32, 2531; Sommer, *ibid.* 1900, 33, 1078; Fournier, Compt. rend. 1901, 133, 635). The *o*-aldehyde has b.p. 200°.

When *m*-tolualdehyde, b.p. 199°, is run into 10 times its weight of fuming sulphuric acid at about 0·5° and the mixture agitated until it is completely soluble in water, m-*tolualdehyde-*o-*sulphonic acid* is formed which is separated by pouring the mixture on ice and neutralising it with barium carbonate. The sulphonic acid yields, with aromatic amines, dyestuffs fast to alkalis (Fr. Pat. 311739 of 1901).

The *p*-aldehyde may be prepared by passing a stream of carbon monoxide and hydrogen chloride into toluene containing aluminium chloride (D. R. P. 98706; Gattermann and Koch, Ber. 1897, 30, 1623). It has b.p. 204°.

p-*Tolualdehyde diacetate* $C_7H_7{\cdot}CH(OAc)_2$ may be formed by the action of acetic anhydride on *p*-tolualdehyde at 150°–180°. It crystallises in colourless glistening leaflets, m.p. 69°, soluble in alcohol and forming a leuco malachite-green when heated with dimethyl aniline and zinc chloride (Claussner, Ber. 1905, 38, 2860).

For additional information on the aldehydes and their derivatives see: Auwers and Keil, Ber. 1905, 38, 1693; Rorive and Tollens, *ibid.* 1907, 40, 3107; Francis, *ibid.* 1909, 42, 2216; Gattermann, Annalen, 1906, 347, 347; Law, Chem. Soc. Trans. 1907, 748; Mascarelli and Russi, Atti. R. Accad. Lincei, 1910, [v.] 19, ii. 239.

TOLUHYDROQUINONE *v.* PHENOL AND ITS HOMOLOGUES.

TOLUIDINES $CH_3{\cdot}C_6H_4{\cdot}NH_2$ are prepared by the reduction of nitrotoluenes in the same way as aniline is obtained from nitro-benzene (*v.* ANILINE; D. R. P. 139457, 144809). The *o*-, *m*- and *p*- isomerides may be separated from one another by a variety of processes. The crude product which consists of about 35 p.c. *para*-, 63 p.c. *ortho*-, and 2 p.c. *meta*- toluidines may be strongly cooled, and the *p*- compound separated by filtration under pressure, or the mixture may be distilled fractionally, or treated with disodium phosphate with which the *p*-toluidine forms an insoluble compound; or it may be treated with hydrochloric and oxalic acids and heated to boiling, the sparingly soluble *p*-toluidine oxalate separates whilst *o*-toluidine hydrochloride remains in solution. But, according to Friswell, the quickest and cheapest method is to separate them by freezing in the presence of water or, better, ice. Under these conditions, the *p*-toluidine forms a hydrate (Walker and Beveridge, Chem. Soc. Trans. 1907, 1797), which can be readily separated from the other isomerides and from which pure *p*-toluidine can be prepared. A full description and figure of the apparatus employed in this process is given in the J. Soc. Chem. Ind. 1906, 258.

The separation of aniline and toluidine is based partly on the different strengths of the bases and partly on the difference in the solubility of their acetyl compounds.

Another method depends on the fact that only those amines in which the para- position is unoccupied can be converted into amino-azo compounds. The mixture is therefore treated with hydrochloric acid and sodium nitrite and the unchanged *p*-toluidine is then distilled off with steam. The successful sulphonation of the amines and also the formation of an additive compound with formaldehyde in the presence of hydrochloric acid also depend on the *p*-position being unoccupied, and these facts can be taken advantage of in the separation of *p*-toluidine (D. R. P. 40424; 37932; 87615; 59775; Lewy, Ber. 1886, 19, 1717, 2728; Wülfing, *ibid.* 2132; Heusserman, Frdl. i. 16; *see* also Schaposchnikoff, J. Russ. Phys. Chem. Soc. 1903, 35, 72; Oglobin, *ibid.* 1904, 36, 680).

p-Toluidine may be detected in the presence of aniline and *o*-toluidine by adding a few drops of ferric chloride to a hydrochloric acid solution of the mixture. If the *p*-compound only is present a Bordeaux red solution is formed. If *o*-toluidine and aniline are present then a greenish-blue precipitate is formed which on filtration gives a red filtrate (Biehringer and Busch, Chem. Zeit. 1902, 26, 1128). Small quantities of *o*- and *p*-toluidines may be estimated by converting them into the dibromoderivatives (Dobriner and Schranz, Zeitsch. anal. Chem. 34, 734). Or the proportion of the *p*- in the *o*-compound may be determined by finding the sp.gr. of the mixture (Lange, *ibid.* 24, 459) or by converting them into their acetyl derivatives and determining the solidification point of the mixture (Holleman, Rec. trav. chim. 1908, 27, 458; Proc. K. Akad. Wentensch, Amsterdam, 1904, 7, 395). For other methods, *see* Häussermann (Zeitsch. anal. Chem. 26, 750); Reinhardt (*ibid.* 33, 90); Raabe (Chem. Zeit. 1891, 15, 116, 179). For the detection and estimation of moisture, *see* Reinhardt, *l.c.*; Dobriner and Schranz, *l.c.*

o-**Toluidine** ($CH_3{:}NH_2 = 1:2$) is a colourless, thick, refractive liquid, with a characteristic odour, and b.p. 199·7°; sp.gr. 1·1012 at 4°/4°, 1·0031 at 15°/15°, 0·997 at 25°/25°, 0·9852 at 50°/50°. When dissolved in sulphuric acid it gives a blue coloration with chromic acid and this on addition of water turns red-violet (Rosenstiehl, Compt. rend. 1868, 67, 398; 1876, 82, 380). A weakly acid solution of *o*-toluidine gives, with a little pure 2 : 5 tolylenediamine and ferric chloride, an intense green coloration. This is a very delicate reaction for *o*-toluidine (Nietzki, Ber. 1877, 10, 1157). When passed through a red-hot tube, *o*-toluidine decomposes into iminoditolyl, ammonia and hydrogen (Seyberth, Ber. 1896, 29, 2594), whilst under the influence of the electric discharge, it gives off little ammonia, but forms a strongly basic polyamine (Berthelot, Compt. rend. 1898, 126, 780). In alkaline solution, it is oxidised with production of an azotoluene, oxalic acid and ammonia, whilst in acid solution it gives rise to quinone derivatives. Azo derivatives are also obtained when it is treated with nitric acid (Nietzki, *l.c.* 662; Ullmann and Forgan, Ber. 1901, 34, 3805; *see* also Bradshaw, Amer. Chem. J. 1906, 35, 326). Its hydrochloride when electrolysed or when treated with potassium dichromate yields dyestuffs (Goppelsroeder, Dingl. poly. J. 1877, 223, 347, 634; Coninck, Compt. rend. 1898, 127, 1221).

o-Toluidine, printed on the fibre, can be oxidised to a moderately permanent dark violet dye by means of sodium chlorate and potassium ferrocyanide; *m*-toluidine is so oxidised to a blackish-violet and *p*-toluidine to a chestnut-brown colour (Kirpitschnikoff, Zeitsch. Farb. Text. Ind. 1905, 4, 233).

o-Toluidine gives precipitates with the salts of the rare metals (Jefferson, J. Amer. Chem. Soc. 1902, 24, 540) and a violet colouring matter with thallium chloride (Renz, Ber. 1902, 35, 2768). It gives a calcium salt $(NHC_7H_7)_2Ca$ (Erdmann and Smissen, Annalen, 1908, 361, 52). When treated with hydrogen in presence of reduced nickel, *o*-toluidine yields methyl *cyclo*hexylamine (Sabatier and Senderens, Bull. Soc. chim. 1904, 31, 769).

o-Toluidine also reacts with diazo compounds (Mehner, J. pr. Chem. 1902, 65, 401); with methylene iodide (Senier and Godwin, Chem. Soc. Trans. 1902, 280); with phenyl urethane (Dixon, *ibid.* 1901, 102); and with phosphoryl trithiocyanate (*ibid.* 541).

When a mixture of *o*-toluidine and *p*-aminophenol in sulphuric acid is oxidised with sodium dichromate, a colouring matter is formed which, with sodium sulphide, yields the leuco base of p-*aminotolyl*-p-*hydroxyphenylamine*

$$NH_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_6H_4{\cdot}OH,$$

m.p. 159°–160° (Gnehm, J. pr. Chem. 1904, [ii.] 69, 161).

o-Toluidine also condenses with a number of aldehydes (Eibner and Peltzer, Ber. 1900, 33, 3460; Fosse, Bull. Soc. chim. 1901, 25, 375; Etard, *ibid.* 1883, 39, 530; Pictet, Ber. 1886, 19, 1063; Sachs and Kempf, Ber. 1902, 35, 2704; Cohn and Blau, Monatsh. 1904, 25, 365; Walther and Raetze, J. pr. Chem. 1902, 65, 258) and forms compounds with the halogen acids and with sulphuric, nitric, phosphoric and phosphorous acids (Ullmann, Ber. 1898, 31, 1699; Städl. Ber. 1883, 16, 28; Wellington and Tollens, *ibid.* 1885, 18, 3313; Lewy, *l.c.*; Hitzel, Bull. Soc. chim. 1894, [iii.] 11, 1054; Lemoult, Compt. rend. 1906, 142, 1193).

o-Toluidine itself and its halogen acid compounds form addition products with metallic halides, sulphates, sulphites and nitrates (Tombeck, Compt. rend. 1897, 124, 963, 1532; Ann. Chim. Phys. 1900, [vii.] 21, 397; Hauser and Vanino, Ber. 1900, 33, 2271; Higbee, Amer. Chem. J. 1900, 23, 150; Stagle, *ibid.* 1898, 20, 640; Base, *ibid.* 653; Swan, *ibid.* 622; Prokojeff, Chem. Zentr. 1897, i. 1028).

It also forms a chloracetate

$$C_7H_9N{\cdot}CH_2Cl{\cdot}CO_2H$$

m.p. 95° (Bischoff, Ber. 1888, 21, 1260); a *benzene sulphonate* $C_7H_9N{\cdot}C_6H_6SO_3$, m.p. 137° (Norton and Westenhoff, Amer. Chem. J. 1888, 10, 135); a p-*toluenesulphonate*, m.p. 180° (Norten and Otten, *ibid.* 144); a *toluene sulphinate* $C_7H_9N{\cdot}C_7H_8SO_2$, m.p. 124° (Hälssig, J. pr. Chem. [ii.] 56, 217); a *trichlorosuccinate* $(C_7H_9N)_2,C_4H_3Cl_3O_4,C_2H_5OH$ which decomposes on heating (Van der Riet, Annalen, 1894, 280, 232); an amidosulphonate $C_7H_9N{\cdot}SO_3H(NH_2)$

m.p. 131° (Paal and Jänicke, Ber. 1895, 28, 3162) and an *ethyl nitrosocyanacetate*

$$2(CN{\cdot}C(CO_2C_2H_5):NOH),C_7H_9N,$$

m.p. 85°–95° (Muller, Ann. Chim. Phys. 1894, [vii.] 1, 516).

m-**Toluidine** ($CH_3:NH_2 = 1:3$) is employed technically only to a limited extent in the production of dyestuffs (D. R. P. 93499, 219210; Monnet, Reverdin and Nölting, Ber. 1879, 12, 445; Rosenthiel and Gerber, Compt. rend. 1882, 95, 238).

It is a colourless oil, b.p. 203·3° (Kahlbaum, Zeitsch. Physikal. Chem. 1898, 26, 621, 648); sp.gr. 1·0041 at 4°/4°; 0·9961 at 15°/15°, 0·990 at 25°/25°. It becomes brown and resinous on standing and closely resembles the *o*-compound in most of its properties, but may be distinguished from the latter by its acetyl derivative, which has m.p. 65·5° (the *o*-acetyl derivative has m.p. 110°). It is also less poisonous to the animal organism than *o*-toluidine (Gibbs and Hare, Amer. Chem. J. 12, 365; Wertheimer and Meyer, Ber. 1891, 24, ref. 162). It may be detected and also estimated by converting it into its dimethyl derivative, which, unlike the corresponding *o*- and *p*- compounds, readily yields a nitroso derivative as a yellow crystalline precipitate, when treated with hydrochloric acid and sodium nitrite (Wurster and Riedel, Ber. 1879, 12, 1796).

m-Toluidine combines with methylene iodide (Senier and Godwin, *l.c.*); with diazo compounds (Mehner, *l.c.*); with chloracetyl urethane (Frerichs and Breustedt, J. pr. Chem. 1902, [ii.] 66, 231); with diphenyl thiocarbamide giving diphenyl-*m*-tolyl guanidine (Alway and Vail, Amer. Chem. J. 1902, 28, 294); with benzylidene acetyl acetone (Ruhemann and Watson, Chem. Soc. Trans. 1904, 1170); and with the cyanhydrin of benzaldehyde forming *a-cyanobenzyltoluidine*, m.p. 97° (Sachs and Goldman, Ber. 1902, 35, 3319).

m-Toluidine behaves like the *o*- compound on oxidation, on hydrogenation, and under the influence of an electric discharge, and it also yields similar addition compounds with acids and with metallic halides (Kraut, Annalen, 1881, 210, 323; Higbee, Chem. Zentr. 1900, i. 720; Slagle, *ibid.* 1898, ii. 1044; Base, *ibid.* 1045).

p-**Toluidine** ($CH_3:NH_2 = 1:4$) was the first of the 3 isomerides known and was at one time termed simply *toluidine* (Muspratt and Hofmann, Annalen, 1845, 54, 1); for various methods of preparation *see* D. R. P. 34234, 83544; Frdl. i. 15; *ibid.* iv. 52, 66. It forms leaflets, m.p. 45°, b.p. 200·4° (Hulett, Zeitsch. physikal. Chem. 1899, 28, 651, 657). When exposed to the air it gradually turns yellow, then brown. It has a burning taste, smells something like aniline, and has a similar physiological action to the other two isomerides, but is not so poisonous as the *o*-compound (Gibbs and Hare, *l.c.*; Wertheimer and Meyer, *l.c.*; Bokornoy, Zeitsch. angew. Chem. 1897, 10, 338; Hildebrandt, Hofmeister's Beitragen Chem. Physiol. and Path. 1903, 3, 372; *ibid.* 1905, 7, 433).

p-Toluidine acts as a very weak base (Walker, Zeitsch. physikal. Chem. 1890, 5, 195; Bredig, *ibid.* 1894, 13, 323; Lowenherz, *ibid.* 1898, 25, 394).

By the action of potassium dichromate on -toluidine sulphate, Perkin (in 1880) obtained two oxidation products $C_{21}H_{21}N_3$ and $C_{28}H_{27}N_5$. Oxidation with lead peroxide leads to one or other oxidation product, depending on the conditions of the experiment. In very dilute solutions the substance with fewer carbon atoms is formed, whilst in concentrated solution the compound of higher molecular weight is obtained (Börnstein, Ber. 1901, 34, 1274).

When treated in sulphuric acid solution with potassium permanganate, *p*-toluidine yields nitroso toluene (Bamberger and Tschirner, Ber. 1898, 31, 1524); whilst with chloroform and calcium chloride, azotoluene is formed (Meigen and Normann, *ibid.* 1900, 33, 2711): the latter is also formed when *p*-toluidine is oxidised with ozone, hydrogen peroxide, or potassium dichromate under certain conditions (Bamberger and Tschirner, *ibid.* 1899, 32, 1677; Otto, Ann. Chim. Phys. 1898, [vii.] 13, 142).

Heated with *aqua regia* it yields chlorotoluene; with hydrogen iodide, it gives toluene. When *p*-toluidine is heated with a *meta*- derivative of nitrobenzene, in the presence of hydrochloric acid, it yields dyestuffs of the chrysaniline series (D. R. PP. 65985, 78377, 79263, 79585, 79877, 81048).

Two parts of *p*-toluidine heated with 1–2 parts of sulphur at 180°, gives rise to the primuline bases (Green, Ber. 1889, 22, 968; Jacobson, *ibid.* 330; Gattermann, *ibid.* 422; Gattermann and Pfitzinger, *ibid.* 1063). Heated with ethyl alcohol and zinc chloride it forms 4-amino-1-methyl-3-ethylbenzene (Willgerodt and Brandt, J. pr. Chem. 1904, [ii.] 69, 433).

p- and *o*-Toluidines condense with bromo and with sulphonated methylamino-anthraquinones forming blue and green dyes (D. R. P. 159129; Wacker, Ber. 1902, 35, 2593; Friedlander and Schick, Zeitsch. Farb. Text. Ind. 1904, 3, 218; see also D. R. PP. 149780, 148767, 153517, 174131).

p-Toluidine also condenses with diazo-compounds (Mehner, *l.c.*); with phenylurethane (Dixon, *l.c.*); with methylene iodide (Senier and Goodwin, *l.c.*); with acetylene tetrabromide (Sabanéeff and Rakovsky, J. Russ. Phys. Chem. Soc. 1902, 34, 408); with phenyl isocyanate (Walther and Stenz, Bull. Soc. chim. 1901, 26, 395); and with epichlorhydrin (Cohn and Friedlander, Ber. 1904, 37, 3034). An additive compound of *p*-toluidine and trinitrotoluene; forms dark red crystals, m.p. 68° (Jackson and Clarke, Chem. Soc. Proc. 1906, 84).

When *p*-toluidine is heated on the water-bath with dichloraceto-*p*-toluidide, *p-methylisatin*-p-*tolylimide* is formed; the action of *p*-toluidine on similar di- and trichloraceto compounds is described by Heller (Annalen, 1904, 332, 247).

When *p*- or *o*- toluidine is diazotised in sulphuric acid solution, then saturated with sulphur dioxide, treated with copper, filtered and washed with ammonia, and the washings and filtrate treated with ferric chloride, the corresponding *ferric toluene sulphonate*

$$Fe(C_6H_4Me{\cdot}SO_2)_3$$

is formed from which the free acid may be readily obtained (Thomas, Chem. Soc. Trans. 1909, 343).

Like the *o*- and the *m*- isomerides, *p*-toluidine forms compounds with the halogen and other inorganic and organic acids, and also double salts with a number of metallic chlorides, and with other salts of both organic and inorganic acids. It yields a calcium salt similar to the *o*- compound (Erdmann and Smissen, *l.c.*).

p-Toluidine condenses with aromatic aldehydes in the presence of its hydrochloride, forming acridines (Ullmann, Ber. 1903, 35, 107); with benzylidene acetone it forms β-tolylaminobenzylacetyl acetone, m.p. 96° (Ruhemann and Watson, Chem. Soc. Trans. 1904, 1170).

For other condensation products of *p*-toluidine with aldehydes, *see* Eibner and Amann, Annalen, 1903, 329, 211; Friedländer, Ber. 1892, 25, 2049; Eibner and Parucker, *ibid.* 1900, 33, 3662; Hantzsch and Schwab, *ibid.* 1901, 34, 822, 841; Cohn and Friedländer, *ibid.* 1902, 35, 1265; Cohn and Blau, Monatsh. 1904, 25, 365; amongst others.

Halogen derivatives of o-*toluidine*. When *o*-toluidine is chlorinated in an excess of 98 p.c. sulphuric acid, a monochlorotoluidine, m.p. 119°–120°, of unknown constitution is formed (Hafner, Ber. 1889, 22, 2535, 2538). In general, the substituted halogen derivatives, of which a very large number are known, may be obtained by the reduction of the corresponding halogen nitrotoluene, as well as by various other methods (Reverdin and Crépieux, Ber. 1900, 33, 2505; Elbs and Silbermann, Zeitsch. Elektrochem. 1900–1901, 7, 590; Cohen and Dakin, Chem. Soc. Trans. 1901, 1127; Nölting, Ber. 1904, 37, 1019).

4-Chloro-2-toluidine has m.p. 21°–22°, b.p. 237°/22 mm. (Goldschmidt and Hönig, *ibid.* 1886, 19, 2441; Cohn, Monatsh. 1901, 22, 473).

5-Chloro-2-toluidine forms lustrous white crystals, m.p. 29·5°–30°, b.p. 245°–246·5°/753 mm. (Wynne, Chem. Soc. Trans. 1892, 1042).

6-Chloro-2-toluidine, colourless oil, b.p. 242°–244°, which rapidly turns brown on exposure to air (Cohn, *l.c.*; Nölting, *l.c.*).

3 : 5-Dichloro-2-toluidine forms long, colourless crystals, m.p. 53° (Claus and Stapelberg, Annalen, 1893, 274, 292).

4 : 5-Dichloro-2-toluidine forms silky plates, m.p. 100°–101° (Cohen and Dakin, *l.c.*).

3 : 4-Dichloro-2-toluidine is known in the form of its acetyl derivative, which has m.p. 158°–159° (Cohen and Dakin, *l.c.*).

Halogen derivatives of m-*toluidine* may be obtained by the reduction of the corresponding nitrohalogen toluene, or by the chlorination of aceto-*m*-toluidide (Bamberger and Werra, Ber. 1902, 35, 3718; Reverdin and Crépieux, *ibid.* 1900, 33, 2503; Cohen and Dakin, *l.c.*).

2-Chloro-3-toluidine, b.p. 228°–229° (Wynne and Greeves, Chem. Soc. Proc. 1895, 151), is an oil volatile in steam.

4-Chloro-3-toluidine (Claus, J. pr. Chem. 1892, [ii.] 46, 29) forms colourless, thin leaflets, m.p. 32°, b.p. 230°/758 mm.

5-Chloro-3-toluidine has b.p. 242°/730 mm. (Hönig, Ber. 1887, 20, 2419).

6-Chloro-3-toluidine forms colourless, long, lustrous needles, m.p. 83°, b.p. 241°–243° (Reverdin and Crépieux, *l.c.*; Chattaway and Orton, Chem. Soc. Trans. 1901, 461).

2 : 5-Dichloro-3-toluidine, m.p. 69°–70° (Cohen and Dakin, *l.c.* 1330).

2 : 6-Dichloro-3-toluidine, m.p. 59°–60°, and the 4 : 5-*dichloro* compound have been prepared by Cohen and Dakin (*l.c.* 1331, 1346).

4 : 6-Dichloro-3-toluidine, m.p. 85°–87° (Seelig, Annalen, 1887, 237, 163; Cohen and Dakin, *l.c.* 1332, 1348).

5 : 6-Dichloro-3-toluidine has m.p. 88°, b.p. 292° (Wynne and Greeves, *l.c.*).

2 : 4 : 6-Trichloro-3-toluidine forms fine white needles, m.p. 77°–78° (Reverdin and Crépieux, *l.c.*; Cohen and Dakin, *l.c.* 1335).

The *fluorine compound* $CFl_3{\cdot}C_6H_4{\cdot}NH_2$ (Swarts, Bull. Soc. chim. Belg. 1898, [iii.] 35, 388) has been prepared.

Halogen derivatives of p-*toluidine*. When *p*-toluidine is chlorinated in 97 p.c. sulphuric acid, it is partly converted into 3-chloro- (chiefly) and 2-chloro- derivatives. The same products, together with 3 : 5-dichloro-*p*-toluidine are obtained in 40 p.c. sulphuric acid. The latter, together with the 3-chloro- and also higher chlorinated products, are obtained by chlorinating aceto-*p*-toluidide (Hafner, Ber. 1889, 22, 2535; Wroblewsky, Annalen, 1873, 168, 196; Lellman and Klotz, *ibid.* 1885, 231, 308; Zincke, Ber. 1895, 28, 3121). Chlorinated products are also obtained when *p*-toluidine is electrolysed in excess of hydrochloric acid (Elbs and Brunschweiler, J. pr. Chem. 1895, [ii.] 52, 559).

2-Chloro-4-toluidine, m.p. 26°, b.p. 237°–238·5° (Lellmann, Ber. 1884, 17, 534), 245° (Wynne and Greeves, *l.c.*).

3-Chloro-4-toluidine, m.p. 7°, b.p. 223°–224° (Cohen and Dakin, Chem. Soc. Trans. 1902, 1324).

2 : 3-Dichloro-4-toluidine has m.p. 40°–42° (Cohen and Dakin, *ibid.*).

3 : 5-Dichloro-4-toluidine, m.p. 60° (Bamberger, Büsdorf and Szolayski, Ber. 1899, 32, 218; Chattaway and Orton, Chem. Soc. Trans. 1900, 789; Cohen and Dakin, *l.c.*).

2 : 3 : 5-Trichloro-4-toluidine is only known in the form of its acetyl derivative, which has m.p. 179° (Cohen and Dakin, *l.c.*).

Various other chlor-toluidines of unknown constitution have been prepared (Seelig, Annalen, 1887, 237, 141, 163; Wroblewsky, *ibid.* 1873, 168, 213; Schultz, *ibid.* 1877, 187, 278).

Bromo and iodo derivatives, as well as mixed bromo-iodo derivatives of the toluidines, have been prepared (Neville and Winther, Ber. 1881, 14, 419; Glassner, *ibid.* 1875, 8, 561; Michael and Norton, Amer. Chem. J. 1, 263; Wroblewsky, Annalen, 1878, 192, 210, 212; Orton and Reed, Chem. Soc. Trans. 1907, 1570; Wheeler, Amer. Chem. J. 1910, 44, 126; amongst others).

The *nitrotoluidines* are obtained by the nitration of the required toluidine or its acetyl derivatives, or by the reduction of the corresponding dinitrotoluene (Bamberger, Ber. 1894, 27, 586; 1895, 28, 399; 1897, 30, 1259).

3-Nitro-2-toluidine forms yellow crystals, m.p. 97° (Zincke and Schwarz, Annalen, 1899, 307, 44).

4-Nitro-2-toluidine forms light yellow prisms, m.p. 107° (Jäger, Chem. Zentr. 1903, ii. 1051; Willgerodt and Kok, Ber. 1908, 41, 2077).

5-Nitro-2-toluidine, yellow crystals, m.p. 129°–130° (Jäger, *l.c.*; Reverdin and Crépieux, Ber. 1900, 33, 2498).

p-Toluenesulphonyl-5-nitro-*o*-toluidine can be obtained by the action of *p*-toluenesulphonyl chloride on a boiling toluene solution of 5-nitro-*o*-toluidine. On reduction it yields the corresponding *p*-tolylenediamine

$$NH_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}SO_2{\cdot}C_7H_7$$

m.p. 150°, the diazonium chloride of which, when treated with excess of sodium acetate solution, yields *p-toluenesulphonyl-p-aziminotoluene* $C_6H_3MeN_3\cdot SO_2\cdot C_7H_7$, a pale yellow substance which decomposes violently at 156°, and gives a red crystalline compound, m.p. 194°, with β-naphthol in pyridine solution (Morgan and Mickelthwait, Ber. 1906, 39, 2869).

6-Nitro-2-toluidine, long yellow silky needles, m.p. 92° (Nölting, *l.c.* 1018; Green and Lawson, Chem. Soc. Trans. 1891, 1014).

3 : 5-**Dinitro-2-toluidine**, small yellow needles, with a bluish or greenish lustre, m.p. 209°–210° (Hoff, Annalen, 1900, 311, 111).

4 : 6-**Dinitro-2-toluidine** depends for its properties on its mode of preparation (Cohen and Dakin, Chem. Soc. Trans. 1902, 26; Holleman and Boeseken, J. 1897, 1753).

5-Nitroso-2-toluidine $MeC_6H_3(NO)NH_2$ is obtained by melting together nitroso-*o*-cresol (1 part), with ammonium chloride (5 parts), and dry ammonium acetate (15 parts) for ½ hour on the water-bath. It forms green needles with a bluish lustre, m.p. 115°–118° (Mehne, Ber. 1888, 21, 731).

Nitro derivatives of m-*toluidine.* When *m*-toluidine is nitrated with nitric acid in concentrated sulphuric acid, it yields chiefly the 6-nitro-derivative, the 2- and 4- derivatives being obtained as by-products (Noelting and Stoecklin, Ber. 1891, 24, 564; Cohen and Dakin, Chem. Soc. Trans. 1903, 331).

2-Nitro-3-toluidine, m.p. 53°, crystallises in yellow needles (Staedel and Kolb, Annalen, 1890, 259, 216).

4-Nitro-3-toluidine (*ibid.* 224) forms gold-yellow tablets, m.p. 110°–110·5° (Cohen and Dakin, *l.c.*).

5-Nitro-3-toluidine crystallises in garnet or brownish-red needles, m.p. 98°–98·4° (Haibach, J. pr. Chem. 1902, [ii.] 65, 242).

6-Nitro-3-toluidine forms long, fine yellow needles, m.p. 137°–138° (Staedel and Kolb, *l.c.*; Cohen and Dakin, *l.c.*).

4 : 6-**Dinitro-3-toluidine** forms small, hard, golden-yellow crystals, m.p. 193°–195° (Hepp, Annalen, 1883, 215, 368; Staedel and Kolb, *ibid.* 1890, 259, 220; Bentley and Warren, Amer. Chem. J. 1890, 12, 1).

2 : 6-**Dinitro-3-toluidine** forms glistening yellow crystals, m.p. 132·5° (Meisenheimer and Patzig, Ber. 1906, 39, 2533).

2 : 4 : 6-**Trinitro-3-toluidine** forms small brownish-yellow crystals, m.p. 138° (Staedel and Kolb, *l.c.*; Noelting and Salis, Ber. 1882, 15, 1864; Blanksma, Chem. Zentr. 1903, i. 78).

6-Nitroso-3-toluidine $MeC_6H_3(NO)NH_2$ is obtained like the corresponding ortho- compound (Mehne, *l.c.*). It forms beautiful steel-blue needles, m.p. 178°.

Nitro derivatives of p-*toluidine.*

2-Nitro-4-toluidine forms yellow glistening broad needles, m.p. 81·5° (Haibach, J. pr. Chem. 1902, ii. 65, 246; Noelting and Collins, Ber. 1884, 17, 263).

3-Nitro-4-toluidine forms red crystals, m.p. 116°–117° (Jäger, *l.c.*; Noelting and Collins, *l.c.*; Noyes, Amer. Chem. J. 1888, 10, 475).

2 : 6-**Dinitro-4-toluidine**, yellow or red crystals, m.p. 171° (Holleman and Boeseken, Rec. trav. Chim. 1897, 16, 425; Beilstein, Ber. 1880, 13, 242).

3 : 5-**Dinitro-4-toluidine**, yellow needles, m.p. 167°–168° (Bamberger and Voss, Ber. 1897, 30, 1257; Niementowski, *ibid.* 1886, 19, 717).

Other dinitro-*p*-toluidines are described by Riggs (Inauguraldissertation Gottingen, 1883); and by Hepp (Annalen, 1882, 215, 371).

A number of halogen nitrotoluidines are also known (Morgan and Clayton, Chem. Soc. Trans. 1905, 944; Beck, Annalen, 1892, 269, 211; Blanksma, Chem. Zentr. 1903, i. 79; Chem. Weekblad. 1909, 6, 717; Wheeler, Amer. Chem. J. 1910, 44, 126; Wheeler and Liddle, *ibid.* 1909, 42, 441; among others).

Sulphonic acid derivatives. When *o*-toluidine is treated with fuming sulphuric acid, or with an acid sulphate, it is converted into the 3-, 4-, or 5-monosulphonic acid, or by further sulphonation, into the 3 : 5- or 4 : 5-disulphonic acids, the predominating product depending upon the conditions of the experiment (Pechmann, Annalen, 1874, 173, 215; Weckwarth, *ibid.* 172, 194; Claus, *ibid.* 1891, 265, 67; Hasse, *ibid.* 1885, 230, 297; Wynne and Bruce, Chem. Soc. Trans. 1898, 734, 743; D. R. PP. 48583, 74111; Reverdin and Crépieux, Ber. 1901, 34, 2993, 2996). A number of halogen and other derivatives of these acids are known.

Sulphonic acid derivatives of m-*toluidine.* When *m*-toluidine is sulphonated with fuming sulphuric acid, 3-toluidine-2-sulphonic acid, which is decomposed at 275° without melting, and the 2 : 4-disulphonic acid, colourless needles are formed (Lorenz, Annalen, 1874, 172, 185).

The 4-sulphonic acid is obtained by the reduction and subsequent debromination of 2-brom-5-nitrotoluene-4-sulphonic acid, the product then being treated with carbon dioxide. Like the other sulphonic acids it yields metallic salts (Hayduck, Annalen, 1874, 174, 350). Halogen, nitro, and other derivatives of these acids are also known.

A sulphonic acid of the constitution

$$SO_3H\cdot C_7H_6\cdot N:N\cdot C_7H_5(NH_2)_2$$

is formed when sulphur dioxide is passed into the cooled liquid obtained on diazotising *m*-toluidine in sulphuric acid solution. The formation of the yellow potassium or sodium salt of this substance is said to be an extremely good indicator for alkalis. The presence of alkali carbonate in tap water may be recognised by this means. With mineral acids it gives a red colour (Tröger and Hille, J. pr. Chem. 1903, 68, 297; *ibid.* 1905, [ii.] 71, 201, 236).

Sulphonic derivatives of p-*toluidine.* *p*-Toluidine is sulphonated with much greater difficulty than the *o*-isomeride, and requires a much higher temperature and more prolonged action, the actual products obtained depending on the conditions of the experiment (Pechmann, Annalen, 1874, 173, 195; Claus and Immel, *ibid.* 1891, 265, 82; Janovsky and Reimann, Ber. 1888, 21, 1216).

4-Toluidine-2-sulphonic acid gives a number of salts, a diazosulphonamide and many other derivatives (Ascher, Annalen, 1872, 161, 8; Jensen, *ibid.* 1874, 172, 233; Heffter, *ibid.* 1883, 221, 208; D. R. P. 103578).

4-Toluidine-3-sulphonic acid, and the 2 : 5- and 3 : 5-disulphonic acids and their salts and many derivatives, as well as some sulphonic toluidines of unknown constitution, have also been prepared (Sell, Annalen, 1863, 126, 155;

Richter, *ibid.* 1885, 230, 314, 331, and many others).

6-Chloro-*p*-toluidine-3-sulphonic acid gives a sparingly soluble diazo derivative which unites with β-naphthol, forming an azo dye which gives sparingly soluble calcium, barium, aluminium, and lead salts of brilliant scarlet hue, scarcely attacked by acids and alkalis, and very fast to light (D. R. PP. 175378, 175396).

Other derivatives of the sulphonated toluidines may also be employed in the preparation of dyestuffs.

Alkyl toluidines. *o*-, *m*-, and *p*-**Methyl toluidines** $C_7H_7NH{\cdot}CH_3$ may be prepared by methylating the corresponding toluidine with dimethyl sulphate (Ullmann, Annalen, 1903, 327, 104; Gnehm and Blumer, *ibid.* 1898, 304, 90).

Methyl-*o*-toluidine and its nitroso- derivatives, m.p. 151°, have been employed in the manufacture of the safranines and of azine dyestuffs (D. R. PP. 90256, 80758; Frdl. iv. 406, 376; Weinberg, Ber. 1893, 26, 307; Bernthsen, *ibid.* 992).

Ethyl-*o*-toluidine formed by the electrolytic reduction of acetyl-*o*-toluidine (Baillie and Tafel, Ber. 1899, 32, 73; Vorländer, *ibid.* 1901, 34, 1462); it has b.p. 214°–216°/737 mm.

Phenyl-*o*-toluidine, m.p. 41°, b.p. 305°/727 mm. is prepared by heating *o*-toluidine with aniline hydrochloride, *ditolylamine*, b.p. 312°, being formed at the same time (Girard and Willm, Bull. Soc. chim. 1876, [ii.] 25, 248; Merz and Paschkowetzky, J. pr. Chem. 1893, 48, 461).

Dimethyl-*o*-toluidine $C_7H_7N(CH_3)_2$, b.p. 184·8° D^{20}_{4} sp.gr. 0·9286 at 20°/4°, is formed by the distillation of trimethyl toluidine hydroxide (Monnet, Reverdin and Nölting, Ber. 1878, 11, 2279).

Phenyl-*m*-toluidine, b.p. 300°–305°, is obtained by heating strongly a mixture of phenylaminocresol with zinc powder (Zega and Buch, J. pr. Chem. 1886, 33, 542).

Dimethyl-*m*-toluidine may be prepared by the interaction of *m*-toluidine and methyl iodide, b.p. 215° (Wurster and Riedel, Ber. 1879, 12, 1797), 208° (Reinhardt and Stadel, *ibid.* 1883, 16, 31).

A number of azo derivatives of dimethyl-*m*-toluidine have been obtained by dissolving it together with a diazotisable amine in hydrochloric acid, and adding the solution to an alkaline solution of sodium nitrite (Samelson, Ber. 1901, 33, 3479).

Diphenyl-*m*-toluidine, b.p. 69°–70°, may be prepared like the *o*- isomeride by the interaction of the corresponding chlorotoluene with potassium diphenylamine (Heussermann, Ber. 1901, 34, 38).

Ethyl-*p*-toluidine, b.p. 217°, is formed by the action of ethyl iodide on *p*-toluidine (Morley and Abel, Annalen, 1855, 93, 311).

Phenyl-*p*-toluidine, m.p. 87°, b.p. 317°–318°/727 mm., is formed by heating bromobenzene with *p*-toluidine and caustic soda at 360°–380° (Merz and Paschkowetzky, J. pr. Chem. 1893, 48, 455).

Benzyl-*p*-toluidine is formed by the action of *p*-toluidine on nitrosobenzylbenzoylaniline (Sachs and Goldmann, Ber. 1902, 35, 3319).

Di-*p*-tolylamine, m.p. 79°, b.p. 328·5°, is formed by heating *p*-cresol with ammoniacal zinc chloride and ammonium chloride at 330°–340° (Merz and Müller, Ber. 1887, 20, 546; Merz and Paschkowetzky, *l.c.*).

Dimethyl-*p*-toluidine, b.p. 209·5°, sp.gr. 0·9287 at 20°/4°, can be formed by distilling trimethyl-*p*-tolyl ammonium hydroxide (Hübner, Tölle, and Athenstädt, Annalen, 1884, 224, 337; *see* also Clarke, Amer. Chem. J. 1905, 33, 496).

Many other alkyl compounds of the three toluidines are known, and also nitro, halogen, and other derivatives of these substances (Pinnow, Ber. 1895, 28, 3041; Gomberg, *ibid.* 1902, 35, 1822; Wedekind and Oberheide, *ibid.* 1904, 37, 2712, 3894; Simanowsky and Menschutkin, J. Russ. Phys. Chem. Soc. 1903, 35, 204; Friedländer and Cohn, Monatsh. 1902, 23, 543; Ber. 1902, 35, 1265; and many others).

The *toluidides* or *toluides* C_7H_7NHR may be prepared by treating the iodomagnesium derivative of the required toluidine with an ester of the required acid (Bodroux, Bull. Soc. chim. 1905, 33, 831; *see* also Compt. rend. 1905, 141, 195; *ibid.* 1907, 144, 1437). The *p*-toluides have also been prepared by heating the sodium salt of the required acid with *p*-toluidine hydrochloride (Amer. Chem. J. 1903, 29, 511), or by heating the acid and amine in a sealed tube at 160°–190° for 8–12 hours (Robertson, Chem. Soc. Trans. 1908, 1036). A number of *o*-, *m*-, and *p*-toluides of inorganic and organic acids have been prepared by these and other methods (Michaelis, Annalen, 1893, 274, 226; Michaelis and Schulze, Ber. 1894, 27, 2578; *ibid.* 1895, 28, 1243; *ibid.* 1896, 29, 726; Reynolds, Chem. Soc. Trans. 1889, 480; Lander, *ibid.* 1901, 690; Cohen and Dakin, *ibid.* 1903, 331; Wheeler, Amer. Chem. J. 1900, 23, 466; Kuhara and Chikashigé, *ibid.* 1902, 27, 1; Ley, Ber. 1898, 31, 241; Niementowski, *ibid.* 1892, 20, 1887; Ullmann and Uzbachian, *ibid.* 1903, 36, 1797; Lumière and Barbier, Bull. Soc. chim. 1905, 33, 784; Just, Ber. 1886, 19, 983; J. Soc. Chem. Ind. 1891, 1000; Orloff, J. Russ. Phys. Chem. Soc. 1905, 37, 439; Taussig, Monatsh. 1904, 25, 375; D. R. P. 183843, 156177, 157103; Ullmann and Gross, Ber. 1910, 43, 2694, amongst many others).

An iso*succinic*-p-*toluide* having a slight antipyretic and hæmolytic action, has been prepared by Malerba (Chem. Zentr. 1906, ii. 349).

For a number of other complex toluidine compounds, *see* Guerin, Bull. Soc. chim. 1903, [iii.] 29, 1117; Morgan and Clayton, *l.c.*; Schroeter, Ber. 1905, 38, 3181; Willgerodt and Simonis, *ibid.* 1906, 39, 269; Ostromisslensky, *ibid.* 1907, 40, 4972; *ibid.* 1908, 41, 3029; Kunckell, *ibid.* 4111; Robyn, Compt. rend. 1905, 140, 1644; Raper, Thompson and Cohen, Chem. Soc. Trans. 1904, 371; D. R. PP. 145189, 181929.

TOLUINDAZINE *v.* AZINES.

TOLUNAPHTHAZINES *v.* AZINES.

TOLUPHENAZINE *v.* AZINES.

TOLUQUINOL. *Toluhydroquinone v.* PHENOL AND ITS HOMOLOGUES.

TOLUSAFRANINES *v.* AZINES.

TOLUSTILBAZINE *v.* AZINES.

TOLUYLENE ORANGE *v.* AZO- COLOURING MATTERS.

TOLYLENE BLUE *v.* INDAMINES AND INDOPHENOLS.

TOLYLENE-DIAMINES. *Diamino-toluenes* v. AMINES.

TOLYLENE RED v. AZINES.

TOLYPYRIN, TOLYSAL, v. SYNTHETIC DRUGS.

TOMATO, *Solanum Lycopersicum* (Linn.) or *Lycopersicum esculentum vulgare.* A Peruvian plant now largely cultivated in many parts of the world for its fruit, which is esteemed as a vegetable. Several species and many varieties are known, differing greatly in size, shape, and colour of fruit.

König gives as the average composition—

Water	Protein	Fat	Sugar	Other N-free extract	Crude fibre	Ash
93·4	1·0	0·2	3·5	0·5	0·8	0·6

About half the total nitrogen is present as true proteids.

Passerini (Staz. Sper. Agrar. 1891, 18, 545) found the fresh fruit to consist of skin 1·3 p.c., pulp and juice 96·2 p.c., and seeds 2·5 p.c., and the pulp to contain two colouring matters —a yellow amorphous substance and a red crystalline compound—both insoluble in water, but soluble in amyl alcohol or ether, and bleached by chlorine. He attributes the acidity to citric acid, which he estimates as forming about 9 p.c. of the total dry matter of the whole fruit. The ash he found to contain—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
59·5	6·0	1·3	3·1	0·2	12·9	3·5	0·3	19·1

Albahary (Compt. rend. 1907, 145, 131) found in the fresh fruit—

Water	Protein	Fat	Carbo-hydrates	Malic acid	Citric acid	Oxalic acid	Ash
93·5	1·0	0·2	3·6	0·49	0·15	0·001	0·74

Traces of tartaric and succinic acids were also detected.

Stüber (Zeitsch. Nahr. Genussm. 1906, 11, 578) obtained somewhat similar results, but states that citric acid was the chief cause of the acidity (amounting to about 0·5 p.c. citric acid), and that he could not detect malic, tartaric, or succinic acids.

The juice of tomatos was found by Passerini (*l.c.*) to have a sp.gr. 1·01833 at 15°, to contain 2·44 p.c. of dry matter, of which rather more than ⅕ was protein, ⅕ ash, and a little more than half carbohydrates and acids.

Other analyses of the juice were made by Stüber (*l.c.*), who found water 96·1, nitrogen 0·093, ash 0·56, total sugars, after inversion, 2·15, acidity (as citric acid) 0·65 p.c. The red colouring matter of the tomato was investigated by Arnaud (Compt. rend. 1886, 102, 1119), who believed it to be identical with carrotene $C_{40}H_{56}$; Montanari (Chem. Zentr. 1905, i. 544) concluded that it had the composition $C_{52}H_{74}$; Willstätter and Escher (Zeitsch. physiol. Chem. 1910, 64, 47), who name it *lycopene*, find that it has the molecular composition $C_{40}H_{56}$, the same as that which Willstätter and Mieg (Annalen, 1907, 355, 1) have ascribed to carrotene. It, however, differs in its properties from that substance. It crystallises from light petroleum or a mixture of alcohol and carbon disulphide in dark, carmine-red, felted prisms; it melts at 168°–169° (corr.), but is less soluble in ether, alcohol, carbon disulphide, or light petroleum than carrotene. It absorbs oxygen much more readily than does carrotene and forms a di-iodide $C_{40}H_{56}I_2$, a dark green, gelatinous, insoluble substance.

The leaves and stems of tomatos were examined by Passerini (Staz. Sper. Agrar. 1893, 20, 471), who found in the fresh substance—

	Total dry matter	Ash
Stems . .	8·8–9·9	1·6–2·0
Leaves . .	11·6–14·6	1·6–3·2

The ash contained—

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	Mn_3O_4	P_2O_5	SO_3	SiO_2	Cl
Stems	25·0	11·1	32·8	7·9	0·8	—	2·3	4·7	6·0	14·5
Leaves	2·0	1·4	38·1	9·0	0·1	0·05	1·4	12·8	33·8	1·8

Lithium, boron, and copper were also present in the ash of the stems.

Salicylic acid occurs naturally in tomatos, although in very small quantity. Pellet (Ann. Chim. anal. 1907, 12, 10) considers that the presence of 10 mgm. of salicylic acid in 1 kilog. of tomatos should not be regarded as proof of adulteration.

Tomatos are often canned. American analyses (Bull. 28, U. S. Dept. of Agric.) give, as the mean of 19 samples—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
94·0	1·2	0·2	3·5	0·5	0·6

In the ash was included about 0·1 p.c. common salt. Tomatos are largely used in the preparation of sauces and chutneys, in some of which the red colour is enhanced by the addition of eosin (König). H. I.

TONITE v. EXPLOSIVES.

TONKA BEAN. *Tonquin bean* (*Fève tonka*, Fr.; *Tonkabohnen*, Ger.). The seed of the fruit of the leguminous tree *Dipterix odorata* (Willd.) which inhabits Guiana and Venezuela. Each pod contains a single seed, which is about 2 ins. long and ⅓ in. wide. It has a dark-brown colour, is deeply wrinkled externally, and characterised by an agreeable odour and bitter aromatic taste. The tree flourishes in the forests of the Caracas district of Venezuela. The first crop of beans is gathered when the tree is three years old, but a full crop is not obtained until two years later. The fruit bears some resemblance to a small mango, and contains the odorous bean in its centre. The seed of *D. oppositifolia* (Willd.), the so-called English Tonka bean, has similar properties to that of *D. odorata*, but it is smaller and darker in colour.

Besides sugar, gum, malic acid, and woody fibre, tonka bean contains *fixed oil* and about 1·5 p.c. of *coumarin* (Boullay and Boutron-Charlard, J. Pharm. Chim. 11, 480). It is to the presence of coumarin that the odour and taste of the seed are due, and crystals of this compound often occur as an efflorescence on commercial specimens. To extract the coumarin, the finely-chopped beans, according to Gössmann, are heated for some time nearly to boiling with an equal bulk of 80 p.c. alcohol; the whole is then filtered and the residue again heated in the same manner; the extracts are mixed together, and the alcohol removed by distillation until the residue becomes turbid, when it is mixed with four times its volume of water, which precipitates the coumarin in somewhat impure crystals. Adhering fat may be removed by heating the mixture to boiling, and filtering through a moistened filter. On cooling, the crystals which re-dissolve in the hot liquid again separate, and they may be further purified, if necessary, by treatment with animal charcoal (Annalen, 98, 66), *v.* Coumarin.

Tonka bean is used to flavour tobacco, and especially snuff, as an ingredient of sachet powder, and in alcoholic solution as a flavouring essence. A. S.

TOPAZ (*Topas*, Ger.). A gem-stone composed of aluminium fluo-silicate $(AlF)_2SiO_4$ crystallised in the orthorhombic system. As shown by S. L. Penfield and J. C. Minor (Amer. J. Sci. 1894, 47, 387) the fluorine (15·48–20·37 p.c.) is replaced isomorphously by hydroxyl (0·18–2·50 p.c., as shown by analyses), so that the formula becomes $[Al(F,OH)]_2SiO_4$; and, chemically, a fluor-topaz and a hydro-fluor-topaz may be distinguished. Although these two varieties show slight differences in sp.gr. (3·574 in the former. and 3·523 in the latter). and in optical constants, the distinction is of no practical importance. The mineral is very resistant to acids, and water is expelled only at an intense heat. Topaz usually occurs as crystals in granitic and gneissose rocks, and is often associated with tin-ore. An important character is the presence of a perfect cleavage in one direction, perpendicular to the prism. The crystals may be dull and opaque, or more often clear and transparent, and colourless, bluish, greenish, yellow, or pink. The sherry-yellow crystals from Brazil become pink when heated ('burnt topaz'). Most of the gem material comes from Brazil and Russia, but it is also found in many other countries. Colourless topaz, when faceted, is sometimes mistaken for diamond, and much yellow quartz ('Spanish topaz,' 'Scotch topaz,' 'occidental topaz') is passed off as topaz. The more valuable yellow corundum, on the other hand, is known as 'oriental topaz.' The distinguishing characters of these are shown in the following table :—

—	Topaz	Quartz 'Occidental topaz'	Corundum 'Oriental topaz'
Comp.	$(AlF)_2SiO_4$	SiO_2	Al_2O_3
Cryst.	Orthorhombic	Rhombohedral	Rhombohedral
Sp.gr.	3·55	2·65	4·0
H.	8	7	9
Refr. indices	1·61–1·63	1·54–1·55	1·76–1·77

L. J. S.

TOPAZ, ORIENTAL, *v.* Corundum.

TOPAZ, SCOTCH, *v.* Cairngorm.

TOPAZ, SPANISH, *v.* Cairngorm.

TORBANITE or **TORBANEHILL MINERAL** *v.* Paraffin.

TORBERNITE or **CUPRO-URANITE** (*Kupferuranit*, Ger.). A mineral consisting of hydrated phosphate of uranium and copper

$$Cu(UO_2)_2P_2O_8,8H_2O.$$

It crystallises in square (tetragonal) plates, which possess a perfect micaceous cleavage, with pearly lustre, parallel to their surface. The colour is bright grass-green, which distinguishes cupro-uranite at a glance from the closely-allied mineral autunite (*q.v.*) or calco-uranite. Sp.gr. 3·5; H. 2½. It is a mineral of secondary origin, occurring in the upper portions of lodes containing pitchblende and copper ores, and sometimes as an incrustation on the joint faces in granite. Fine specimens have been found at Gunnislake, Grampound Road, and Redruth in Cornwall. Other localities are Joachimsthal in Bohemia, Johanngeorgenstadt in Saxony, Sabugal in Portugal, &c. To a limited extent the mineral has been mined, together with autunite, as a source of uranium and radium. L. J. S.

TORMENTILLA. The underground stems of *Potentilla Tormentilla* (Neck.) have been occasionally substituted for those of rhatany in medicine. They contain from 5 to 6 p.c. of a tannin, giving a dark-green precipitate with ferrous sulphate, bluish-red with ferric acetate; is also precipitated by gelatin and by tartar-emetic (Stenhouse) (*v.* Tannins).

TORREFACTION. Roasting ores in order to expel volatile substances, *e.g.* sulphur, arsenic, &c.

TOULOUCOUNA or **TULUCANA OIL.** An oil obtained by pressing the kernels of *Carapa Guianensis* (Aubl.), *v.* Carapa oil.

TOULOURON OIL. A brown oil obtained from *Pagarus Latro.* Used in Senegal as a remedy for rheumatism.

TOURMALINE (*Turmalin*, Ger.; from the Cingalese *turamali*). A complex boro-silicate of aluminium, together with variable and mutually-replaceable amounts of ferrous oxide, magnesia, and alkalis. As chemical types there may thus be distinguished iron-tourmaline, magnesium-tourmaline, and alkali-tourmaline. Analyses show: SiO_2, 35–38; TiO_2, 0–1; B_2O_3, 9–11; Al_2O_3, 30–42; Cr_2O_3, 0–10 (rarely); Fe_2O_3, 0–6; FeO, 0–17; MnO, 0–2; MgO, 0–14; CaO, 0–2; Na_2O, 0–3; K_2O, 0–2; Li_2O, 0–1·7; H_2O, 1–4; F, 0–1 p.c. Many different formulæ have been suggested. Penfield and Foote (1899) regard the several varieties as salts of the hypothetical alumino-boro-silicic acid

$$H_9Al_3(BOH)_2Si_4O_{19}.$$

With these wide differences in chemical composition, the sp.gr. ranges from 3·0 to 3·2, and the refractive indices (Na) $\epsilon=1·6123–1·6515$, $\omega=1·6315–1·6854$ (E. A. Wülfing, 1900), but there are only very slight variations in the crystallographic constants (this being attributed by Penfield and Foote to the mass effect of the large acid radicle). The crystals are rhombohedral-hemimorphic, there being a different development of faces at the two ends. The habit is almost invariably prismatic, with deeply-grooved prism faces; the cross-section of the prism is triangular with straight or curved outlines. These peculiarities of form render tourmaline a mineral readily recognisable. As a consequence of the hemimorphism the crystals are pyroelectric. The material ranges from colourless to jet-black in colour, and may be any shade of red, yellow, green, or blue. In one and the same crystal there are often striking contrasts in the differently coloured zones. The more darkly coloured crystals are strongly dichroic, the ordinary ray vibrating perpendicular to the principal axis being almost completely absorbed. On this property depends the use in polarising apparatus (*e.g.* the well-known tourmaline-tongs) of tourmaline plates cut parallel to the principal axis of a crystal.

Common black tourmaline (*schorl*) is of abundant occurrence in granitic and metamorphic rocks, and is a frequent associate of tin ores. Coloured tourmalines are much used in jewellery, either as clear faceted stones or, when cloudy, as beads (H. 7½). The red is often called *rubellite*, and the blue *indicolite*, whilst fanciful names such as 'Brazilian emerald,' 'Siberian ruby,' &c., are also sometimes used. Within recent years large quantities of gem material have been quarried from the pegmatites of California and Madagascar. L. J. S.

TOUS-LES-MOIS is a species of arrowroot procured from the tubers of *Canna edulis* (*Ker-Gawl.*) nat. ord. *Marantaceæ*. The starch is obtained in the same manner as other descriptions of arrowroot. Under the microscope the granules show themselves to be unusually large, measuring from 0·0015 to 0·0037 inch in length and from 0·001 to 0·0027 in breadth; broad, flat, ovate. The hilum is situated at the narrow extremity, and the rings are very close, firm, and regular.

Tous-les-mois is used in admixture with cocoa preparations and as a food for infants, for which latter purpose it is bleached. *V.* Starch.

TOXINS and **ANTITOXINS.**

Toxins.

Infective diseases of man and animals, that is diseases which are contagious, infectious, or transmissible by inoculation, are caused by pathogenic (*i.e.* disease-producing) living organisms which are parasitic on or in the individual attacked. The parasitic organisms may be minute vegetable ones, principally bacteria, minute animal protozoa, or higher and larger forms such as moulds, insects, and worms. The bacteria, and presumably also the protozoa, as a rule produce their deleterious effects principally by means of substances which are poisonous to the host, and which are elaborated by, or are derived from, the parasitic organisms. Even the larger parasites, such as worms, though acting mechanically and in other ways, may also elaborate poisonous substances.

In the early days of bacteriology, under the influence of the work of Panum, Selmi, Nencki, and others on the products of putrefaction, attempts were made to isolate from the cultures of the pathogenic organisms and from the tissues of the disease-stricken patients nitrogenous bodies of a basic and alkaloidal nature similar to the ptomaines of putrefaction, and Brieger in particular isolated such substances as typhotoxine from cultures of the typhoid bacillus and tetanine from the tissues of a case of tetanus (*see* art. Ptomaines). It was soon found, however, that such basic substances are not, as a rule, the essential or specific toxic agents of the pathogenic bacteria, and some of those described by Brieger are quite likely artifacts, due to the methods of extraction employed.

The specific toxic agents of the bacteria, or *toxins*, as they may conveniently be termed, are substances of complex composition, which, so far as they have been investigated, seem occasionally to be protein in nature, or to be allied to the proteins or to the enzymes. The whole subject of the nature of toxins is still in a very indeterminate condition, so that any views expressed here must be regarded as tentative. In some instances the toxin appears to be a substance *sui generis*, in others it may be proteose in nature (tox-albumose), and in others it may be albuminous (tox-albumin). The toxin may be an excretory product, as it were, of the micro-organism, *e.g.* tetanus toxin (S. Martin), or may be formed by the action of enzymes, excreted by the micro-organism, on the constituents of the culture medium or of the tissues, *e.g.* anthrax toxin, or it may be a mixture of these two, *e.g.* diphtheria toxin (S. Martin), or it may be a protein or other constituent of the bacterial cells themselves, *e.g.* typhoid toxin. Toxins which are excretory products, or are formed by the action of the organism on the culture medium, are termed exo-toxins or simply toxins, *e.g.* diphtheria, tetanus, and botulismus toxins; those which are intimately associated with the bacterial cells are termed endo-toxins; the toxins of the majority of pathogenic bacteria belong to the latter class. The term toxin has also been extended so as to include various toxic bacterial extracts, such as tuberculin, the toxic proteins, &c., which are found in the higher plants and animals, *e.g.* abrin and ricin of the jequirity and castor-oil beans respectively, substances like eel serum, which is toxic on injection into other animals, and snake venom.

The bacterial exo-toxins may be prepared by cultivating the organisms in a suitable fluid culture medium under appropriate conditions for 1–4 weeks, and then filtering the fluid culture through a Pasteur-Chamberland porcelain, or a Berkefeld, filter. The filtrate is more or less toxic, and may be termed the toxin broth, the actual toxin contained in it may be concentrated in various ways, but extraction in a pure condition is at present impossible, owing to the difficulty of separating it from the constituents of the culture medium. Bacterial endo-toxins may be obtained by growing the organisms on a solid culture medium and extracting the bacterial mass with weak alkalis, &c., or by grinding up the bacterial paste in a mechanical disintegrator, such as Macfayden and Rowland's or Barnard's, and subsequent filtration through a porcelain filter (Proc. Roy. Soc. 1902 and 1911).

The bacterial toxins generally are unstable bodies, disappearing, or being converted into non-toxic modifications, on keeping, and destroyed by light, warming to 60°–70°, by acids, alkalis, and oxidising agents, and by digestive enzymes; owing to the last-named fact, the toxins usually are not toxic when taken by the mouth, but only on inoculation. They are much more stable in the dry condition than when in solution. They are insoluble in, and are precipitated by strong alcohol, and are precipitated on saturation of their solutions with ammonium sulphate. Diphtheria and tetanus toxins dialyse very slightly through parchment, and they will pass through a gelatin-coated porcelain filter, which does not permit of the passage of serum albumin, suggesting that their molecules are smaller than those of the latter (Brodie, Journ. Path. and Bacter. 1897). They are probably lævorotatory. The 'toxin,' in some instances at least, may contain more than one toxic constituent.

Diphtheria toxin was first investigated by Löffler. By precipitating broth cultures of the diphtheria bacillus with alcohol, he obtained a white toxic powder which he classed among the enzymes (Deut. med. Woch. 1890, Nos. 5 and 6). Roux and Yersin, by the cautious addition of calcium chloride, obtained the toxin entangled with the precipitate of calcium phosphate which comes down, and similarly regarded it as an enzyme (Ann. Inst. Pasteur, iii.). Brieger and Fränkel concluded that the toxin is a protein ('tox-albumin'); they found that it is precipitated by ammonium sulphate, but not by magnesium sulphate, contains a relatively high percentage of sulphur and gives the biuret and Millon's reactions (Berl. klin. Woch. 1890, 241, 1133).

Brieger and Fränkel's method of preparing the diphtheria toxin was to saturate broth cultures with magnesium sulphate at 30°, filter from the precipitated globulin, &c., saturate the filtrate with ammonium sulphate at 30°, wash and dissolve the precipitate, dialyse to remove as much adherent salts as possible, and remove remaining traces of ammonium sulphate by the cautious addition of barium chloride; evaporate the filtrate to half the volume *in vacuô* at 40°, and precipitate with absolute alcohol. The precipitate was collected, redissolved, and precipitated with alcohol 6–8 times. Ultimate analysis gave the following figures: C 45·35, H 7·13, N 16·33, S 1·39, O 29·80.

Brieger and Boer subsequently prepared the diphtheria toxin in as pure a form as it has yet been obtained by precipitating broth cultures with a 1 p.c. solution of zinc sulphate or chloride. The precipitate of the zinc double salt is washed with feebly alkaline water and decomposed with carbon dioxide. The purified product gave the xanthoproteic, biuret, Adamkiewicz's, and Millon's reactions. A litre of broth culture gave about 3 grm. of the zinc double compound (Zeitsch. Hygiene, xxii. 267).

Sidney Martin isolated from diphtheritic membrane and from the spleen and other organs of diphtheria cadavers proteoses, chiefly deutero-albumose, and from the membrane alone an organic acid which was not identified. The latter is a yellowish amorphous body, becoming deep brown with alkalis, and is soluble in water and absolute alcohol, but not in ether, chloroform, or benzene. The proteoses were extracted by placing the minced tissues in absolute alcohol until the ordinary proteins were coagulated and rendered insoluble, extracting with water, and precipitating this extract with alcohol many times. Similar proteoses were obtained from cultures in alkali-albumin of the diphtheria bacillus (Brit. Med. Jour. 1892, i.).

Ehrlich concluded that the diphtheria 'toxin' contains two or more toxic constituents, as well as non-toxic bodies, 'toxoids,' derivatives, or degradation-products, of the toxin (*v. infra*, under *Antitoxins*).

Tetanus toxin was obtained in a somewhat concentrated form by Kitasato from anaërobic broth cultures of the tetanus bacillus (which produces lock-jaw), and he gave a detailed account of the action of heat and of a number of chemical reagents on the toxin broth (Zeitsch. Hygiene, x. 267). Brieger and Cohn precipitated veal-broth cultures by saturation with ammonium sulphate (*ibid.* xv. 1). The toxin formed a flocculent precipitate which floated; it was purified by redissolving, precipitating the protein with basic lead acetate, removing other soluble impurities by dialysis, and finally precipitating the dialysed solution with alcohol. Thus prepared, the tetanus toxin formed pale yellow, odourless, easily soluble scales, having a gummy taste. The solution was feebly lævorotatory. It contained only a trace of ash, but did not give the Millon's and xanthoproteic reactions, and gave no precipitate with potassium ferrocyanide and acetic acid, nitric acid, or mercuric chloride. Boiled with ferric chloride it gave no red colour. With copper sulphate and sodium hydroxide it gave a slight violet colour. It contained no phosphorus and only a trace of sulphur, and ultimate analysis gave the following figures: C 52·08, H 8·1, N 15·71 (Brieger, Zeitsch. Hygiene, xix. 101). Subsequently, Brieger and Boer obtained the toxin by the method employed by them for isolating the diphtheria toxin (*vide ante*). On these facts Brieger considered that the tetanus toxin is not a true protein.

Hayashi, however, employing the Brieger-Boer method, or a modification of it, came to the conclusion that the tetanus toxin is a protein, and is a primary proteose (Arch. f. exper. Pathol. xlvii. 9). S. Martin also isolated proteoses, chiefly deutero-albumose, from the spleen of a cadaver, but they did not induce tetanic convulsions on inoculation. Tetanus cultures contain methyl-mercaptan and other sulphur compounds (Nencki, Monatsh. x.); but Fermi and Pernossi were unable to extract any basic substance from them (Zeitsch. Hygiene, xvi. 385). Besides the convulsive constituent, 'tetano-spasmin,' the toxin broth also contains a substance, 'tetano-lysin,' which is a solvent for red-blood corpuscles. The purified tetanus toxin is probably the most toxic substance known, less than 0·5 mgrm. being a fatal dose for a man.

Anthrax toxin. Hankin obtained proteoses from cultures of the anthrax bacillus, and Brieger and Fränkel a tox-albumin from animals dead of anthrax. Marmier, by precipitating cultures with ammonium sulphate, isolated a toxic substance which he considered to be neither protein nor basic (Ann. Inst. Pasteur. ix. 533). S. Martin (*l.c.*) obtained both from cultures in alkali albumin, and from animals dead of anthrax, proteoses, chiefly deutero-albumose, and a nitrogenous basic substance, both of which were toxic. The toxins are formed mainly by the action on the culture medium of enzymes excreted by the bacillus. Endo-toxins may also be formed.

The toxins of the majority of other pathogenic bacteria are endo-toxins. That is to say, if the organisms be grown in a fluid medium, the filtrate is almost non-toxic, but the dead and disintegrated bacterial cells yield toxic substances. Toxins of protozoan organisms are not known with certainty.

Tuberculin. The original or *old* tuberculin of Koch is obtained by boiling, concentrating over a water-bath and filtering glycerin broth cultures of the tubercle bacillus. It is toxic to healthy animals only in large doses, but minute doses cause considerable disturbance in tuberculous patients and animals, and this reaction is made use of for the detection of tuberculous infection. It contains small quantities of proteoses, extractives, and salts, and traces of basic bodies. Small quantities of an acid substance, probably teraconic acid, possibly derived from the bacillar cells, are also present in cultures of the tubercle bacillus. Other tuberculins and bacterial extracts have been prepared.

It must be clearly recognised that in those cases in which the toxin is supposed to be a proteose or other protein, the latter may be merely constituents of the culture medium by which the toxin is entangled or adsorbed.

[On toxins, &c., *see* Oppenheimer in Kolle and Wassermann's Handbuch der Pathogenen Mikroorganismen, vol. i. (Bibliog.); Vaughan and Novy, Cellular Toxins, 1902 (Bibliog.); S. Martin, Man. of Gen. Pathology, 1904, and Reps. Med. Off. Loc. Gov. Bd. 1889–1900; also various papers in the Ann. Inst. Pasteur; Zeitsch. Hygiene, Centr. Bakteriol. Abstracts also in chemical journals.]

Snake venom. Poisonous snakes are divided into two groups, the colubrine and viperine. The venom, which is secreted by glands in connection with the mouth, may be limpid or syrupy, pale yellow, orange or greenish in colour, odourless and tasteless, sp.gr. 1·04 (rattlesnake), 1·11 (cobra), 1·08 (Russell's viper). Microscopically, it contains few elements, and when dry resembles dry albumin. The reaction of the pure venom is acid; it contains C, H, O, N, and S in the proportions found in proteins, gives the protein reactions, is precipitated with alcohol, ammonium sulphate, sodium chloride, and coagulates on heating. Viperine venoms lose their toxicity on heating to 80°–85°, but colubrine venoms require to be heated to 120° to destroy their toxicity. The active toxic substances of venom are coagulable protems (globulin), proteoses, toxins allied to bacterial toxins, and Faust has separated a non-nitrogenous toxic substance, *ophiotoxin*. The proteoses are chiefly proto- and hetero-proteose. The venoms are complex mixtures containing some, but not in any venom all, of the following active substances: 1. *Neurotoxins* acting on (*a*) respiration, (*b*) heart, (*c*) muscle, particularly the diaphragm; 2. *Cytolysins*, solvents for (*a*) blood corpuscles, (*b*) vascular endothelium, (*c*) other cells; 3. *Fibrin ferment* inducing blood-clotting, and others. The venoms thus produce paralysis of voluntary muscles and of the heart and respiration, solution of the red- and white-blood corpuscles and hæmorrhages, and the blood may be either fluid or coagulated in the vessels, and the bodies of the dead putrefy rapidly owing to the destruction of the anti-bacterial properties of the blood. The venom is most active when injected into a blood-vessel, whereas in the subcutaneous tissues it may take some time to act: it is also readily absorbed from the eye. Taken by the mouth, provided there are no cracks or abrasions, colubrine venom is harmless, but viperine venom may cause gastritis, &c., and even death. The hæmolysins which cause solution of the red-corpuscles are of the nature of 'amboceptors,' requiring a 'complement' (*v. infra* under *Bactericidal sera*) to activate them. In some cases the venom alone can hæmolyse *washed* red-corpuscles *in vitro*, *e.g.* man, dog, &c., in others it has no action on *washed* corpuscles but becomes active on the addition of serum. Some corpuscles, therefore, ontain the activating 'complement,' others do ot, and, hence, are not hæmolysed when washed. Kyes, Sachs, Flexner, and Noguchi have shown that lecithin and lecithides in the corpuscles are the complement-like activators of the hæmolytic amboceptors. A venom which is inactive on washed corpuscles becomes active on the addition of lecithin or even of oleic acid or other fatty acids and soaps.

By the cautious treatment of an animal with increasing doses of venom an antitoxin ('antivenin') is formed which has the power of neutralising the particular venom.

The venom of scorpions (against which an antitoxin can be prepared) and spiders is probably protein in nature; of mosquitos and gnats it may be the products of certain bacteria or moulds present in the œsophageal sacs; of bees a protein-free organic base. The formic acid present in the 'venom' of ants, bees, &c., is probably not the active toxin. Many fish are also poisonous by their bites or by spines connected with special glands. Toads and salamanders have acid and basic poisons in the skin glands. Jelly-fish and sea-anemones have stinging glands. Extracts of intestinal worms may be toxic.

[On snake venom, *see* Martin and Lamb in Allbutt and Rolleston's System of Med. vol. ii. pt. ii. (Bibliog.); Sc. Memoirs of the Gov. of India, Nos. 1, 3, 4, 5, 7, 10, 16, 17; Faust, Die Tiereschen Gifte (Braunschweig, 1906, Bibliog.); Noguchi, Journ. Exper. Med. viii. and ix.; and Snake Venoms (Smithsonian Inst. Publication); Calmette, Venoms and Venomous Animals (Bale). On other animal toxins, *see* Castellani and Chalmers, Manual of Tropical Med. (Bibliog.).]

ANTITOXINS.

It is a remarkable fact that proteins on injection into a suitable animal (the domestic mammals generally) give rise to the formation of 'anti-bodies'—substances having properties in some way opposed to those of the proteins injected—which accumulate in the blood of the treated animal. This property of generating anti-bodies, according to Abderhalden, is characteristic of the animal body and is most active against injected cells, proteins, and allied substances. The substance which generates the anti-body is termed the 'antigen.' If a protein such as human serum is injected into a rabbit, the serum of the treated rabbit gives a white precipitate when mixed with human serum, and to a less extent with apes' serum, but with no other sera—a specific 'precipitin' for human serum has been formed. By this means blood-stains, flesh, &c., can be identified with great certainty. By injecting an enzyme, such as rennin, anti-enzyme is formed which inhibits the action of the enzyme; by injecting red-blood corpuscles 'hæmolysin,' solvent for red-blood corpuscles, is formed. If a poisonous protein is injected (in properly graduated doses so as to avoid killing the animal), such as ricin or snake venom, an anti-body is generated which completely neutralises the poisonous action of the substance injected. The same is the case with toxins like diphtheria and tetanus toxins. By repeated injections of a horse with increasing doses of the toxin, the animal becomes less and less susceptible, so that it can finally tolerate huge doses of the toxin without harm, and coincident with the development of this insusceptibility antidotal substances appear in its blood, and may be obtained in the blood-serum by bleeding the animal and allowing the blood to clot. The antidotal or neutralising substance to toxin is termed antitoxin; it is a fairly stable substance, and by obtaining and bottling the serum aseptically it may be preserved, and is employed to treat the respective disease in man.

The antitoxic serum contains a variable amount of the antitoxic constituent and for therapeutic use must be standardised.

The antitoxic constituent is probably protein (globulin) in nature, or at least is associated with the globulin constituent of the serum. The globulin content of the blood of antitoxin-yielding horses is frequently higher than normal, and the antitoxin may be precipitated by saturation of the serum with magnesium sulphate, or by partial saturation with ammonium sulphate; it comes down with the eu-globulin fraction of the serum globulin.

Brieger and Boer (*l.c.*) separated the antitoxic constituent by the following methods: (*a*) 4 grms. of potassium iodide or chloride are added to 10 c.c. of the antitoxic serum diluted with an equal quantity of distilled water. After solution, 4–5 grms. of finely-powdered sodium chloride are added, the mixture is kept at 30°–37° for 18–20 hours, and the precipitate (0·4 grm.) is collected; it is the antitoxic portion of the serum with a slight admixture of protein and salts.

(*b*) The proteins of the antitoxic serum are precipitated with basic lead acetate containing a trace of ammonia, the precipitate is filtered off and the filtrate is saturated with ammonium sulphate. The precipitate is collected and redissolved, the solution is dialysed, and evaporated to dryness. A light powder is obtained (0·06 grm. from 10 c.c. serum) which contains the antitoxic constituent.

(*c*) 10 c.c. of the serum are diluted with 50 c.c. of distilled water, and 20 c.c. of a 1 p.c. solution of zinc sulphate or chloride are added. The precipitate is collected, dissolved in feebly alkaline water, and the zinc compound is decomposed with carbon dioxide. The antitoxic constituent is present in solution when the precipitant is zinc chloride, but is entangled in the zinc carbonate precipitate when the precipitant is zinc sulphate.

Dzerzgowski and Predtétchensky have elaborated a very exact method by partial saturation of the serum with ammonium sulphate, whereby practically the whole of the antitoxin may be concentrated and recovered from a weak antitoxic serum (Archives des Sc. Biologiques, St. Petersbourg, xvi.).

Anti-venin, the antidotal serum for snake-bites, is a truly antitoxic serum.

In the case of pathogenic micro-organisms which do not form an exo-toxin, an antidotal anti-serum can also be prepared by the injection of the bacterial cells, first killed cultures, and subsequently the living organisms, but such serums are not nearly so potent as the antitoxic serums produced by exo-toxins, and many are practically useless for treating the respective diseases, *e.g.* typhoid and cholera serums. The principal action of such an anti-serum is bacteriolytic, *i.e.* it brings about solution of the microorganism.

In this bacteriolytic reaction (and similarly in the solution of red-blood-corpuscles by a 'hæmolytic' serum) two protein substances seem to be concerned. The fresh anti-serum is solvent for bacteria, but not the old, nor the heated (to 56°C.) anti-serum. The two latter may be rendered active again by the addition of *fresh normal* serum. That is to say, by injection of the bacteria (or blood corpuscles), a new and relatively stable substance is formed, which reacts with an unstable normal constituent of the serum, the two together bringing about bacteriolysis (or hæmolysis). To the former, the name of 'immune body' or 'amboceptor,' to the latter, 'alexin' or 'complement,' is given.

Specificity is the distinguishing feature of the anti-bodies; the anti-body produced by an antigen always reacts most actively with this particular antigen.

The formation of anti-bodies is usually explained by Ehrlich's 'side-chain theory.' This supposes that the protoplasmic molecules of the cells of the animal have an affinity for the substance injected (the 'antigen') which gives rise to the anti-body, so that the antigen becomes incorporated with the protoplasm. The union of the antigen with the protoplasm is assumed to be brought about by the combination of atomic groups comparable to the side-chains of a ring nucleus, those of the protoplasmic molecule being termed 'receptor groups,' those of the antigen 'haptophore (=binding) groups.' The poisoning caused by a toxin is thus due to the union of the toxin with the protoplasm by the combination of the haptophore groups of the toxin with the receptor groups of the protoplasm. Should the animal's protoplasm not possess receptor groups having an affinity for the haptophore groups of the toxin, the toxin would not be poisonous to this animal. This is often the case—a toxin is never poisonous to all animals. Now Ehrlich assumes that the protoplasmic receptor groups fulfil physiological functions in the animal, *e.g.* nutrition, &c., so that when a toxin becomes united with the protoplasm a defect is created, whereby the latter cannot properly fulfil its physiological functions. Provided the dose of toxin be not too large, recovery ensues, due to the regeneration by the protoplasm of the particular receptor groups involved. This process is repeated again and again, and as a result of the continued stimulation by the numerous doses of toxin, the protoplasm ultimately forms the receptor groups in question in large excess—much more than is necessary simply to repair the damage done. A considerable proportion of the now very numerous receptor groups then becomes detached from the protoplasm, accumulates in the blood, and constitutes the anti-body. The antidotal property of antitoxin is, therefore, due to the fact that it saturates the haptophore groups of the toxin so that the latter is then unable to combine with the protoplasm.

[On antitoxins, &c., *see* Ehrlich, Die Wertbemessung des Diphtherieheilserums. 1897; Trans. Jenner Inst. of Prev. Med. ii.; Croonian Lect. Roy. Soc. Lond. 1900; and Collected Papers on Immunity, 1909; Hewlett, Serum and Vaccine Therapy, Churchill, 1910 (Bibliog.); Emery, Immunity and Specific Therapy (Lewis, 1909, Bibliog.).]

Toxin-antitoxin reaction. The neutralisation of toxin by antitoxin is approximately quantitative, and the toxin and antitoxin unite. This is shown by the fact that if a recently-made mixture of toxin and antitoxin be filtered through a gelatin-coated porcelain filter, the toxin passes through into the filtrate, but not the antitoxin (*see ante*). If, however, the mixture be allowed to stand so that interaction may occur, the toxin can no longer be separated from the antitoxin by this method. The interaction between the two is slow, is retarded by cold, and is hastened by warming (Brodie, *l.c.*; Martin and Cherry, Proc. Roy. Soc. Lond. lxiii.).

The exact nature of the union of toxin with antitoxin, 'the toxin-antitoxin reaction,' has been the subject of much controversy, and three principal hypotheses have been formulated to explain it. Ehrlich held that the union is comparable to the combination of a strong acid with a strong base, *i.e.* the reaction is a complete one, and there cannot be at the same time in a mixture of toxin and antitoxin, free toxin and antitoxin, together with neutralised toxin. The strictly quantitative relation of toxin and antitoxin supported this view, viz. if 10 equivalents of antitoxin exactly neutralise 10 equivalents of toxin, then 100 equivalents of antitoxin will exactly neutralise 100 equivalents of toxin. But it is found that if 100 fatal doses of toxin (for the guinea-pig) are just neutralised by 100 equivalents of antitoxin, 101 fatal doses of toxin + 100 equivalents of antitoxin is *not* a fatal mixture, and generally 108–116 (sometimes many more) fatal doses of toxin must be added to the 100 equivalents of antitoxin to render the mixture a fatal one (the Ehrlich phenomenon). Ehrlich explained this by supposing that the 'toxin broth' contains not one toxic substance only, but is a mixture of toxin and toxone, the latter being much less toxic than toxin, though requiring as much antitoxin to neutralise it as toxin does. Toxin has, however, a greater affinity for antitoxin than toxone has, so that when more toxin is added to a neutral mixture of toxin and antitoxin, the toxone-antitoxin complex in the latter is dissociated, and the antitoxin so set free then combines with the added toxin, and it is not until the added toxin is more than can be neutralised by the freed antitoxin that the mixture becomes fatal. Ehrlich, in fact, was forced to conclude that toxin broth contains diverse toxic bodies. The second hypothesis, that of Arrhenius and Madsen, while admitting that the union of toxin with antitoxin takes place in definite proportions, regards it as comparable to the neutralisation of a weak base by a weak acid, *e.g.* ammonia and boric acid, the reaction is incomplete, though resulting in equilibrium, so that free toxin and antitoxin exist in the mixture, together with the toxin-antitoxin complex. The quantity of free toxin would be a function of the relation existing between the initial quantities of the two substances. The Ehrlich phenomenon is quite explicable on this hypothesis, and there is no need to postulate the existence of toxone or other toxic constituents in toxin broth. But other phenomena concerning the neutralisation of toxin by antitoxin do not seem explicable by either of these hypotheses. One of these is what is known as the 'Danysz effect,' which is obtained with many different toxins and their corresponding antitoxins. If a mixture consisting of *a* parts of toxin and *b* parts of antitoxin is exactly neutral, when the whole of the toxin *a* is mixed with the antitoxin; a similar mixture of *a* parts of toxin and *b* parts of antitoxin, prepared by adding the toxin in several fractions to the antitoxin is *still toxic*. This is explained according to Arrhenius and Madsen as being analogous to the neutralisation of chloracetic acid by sodium hydroxide. If equivalent quantities of the acid and base are taken, and only half the acid is added in the first instance to the whole of the hydroxide, the acid is wholly neutralised, leaving half the base free. This then slowly reacts upon the sodium chloracetate forming sodium chloride and glycollate, and the solution ultimately becomes neutral. (Communications from the Nobel Institute, 1, iii. 1906.) The Danysz effect has its counterpart in the neutralisation of arsenious acid with ferric hydroxide. Bordet maintains that the union of toxin with antitoxin takes place in variable proportions, and resembles the phenomenon of adsorption, similar to the colouring of filter-paper with a dye. Thus, if pieces of filter-paper be placed in a dilute solution of a dye at sufficiently long intervals, the first pieces become distinctly coloured, but the last pieces remain colourless through lack of free dye in the solution. On the other hand, if all the pieces of paper are simultaneously placed in the solution, they all become similarly coloured. Likewise, a mixture of toxin and antitoxin, in which the latter is in insufficient quantity to render the mixture completely innocuous, does not contain, according to Bordet, a certain quantity of free toxin, together with neutralised toxin, but contains only molecules of toxin insufficiently neutralised, because the antitoxin is diffused over all the molecules of toxin, each of which, therefore, fixes an amount of antitoxin too small completely to inactivate it. In a series of mixtures containing increasing quantities of antitoxin for a uniform amount of toxin, each molecule of the latter will, therefore, be united to increasing quantities of antitoxin. The toxicity of the poison will thus become weaker and weaker, and such a series of mixtures will possess all degrees of toxicity. From this conception, reversibility of the toxin-antitoxin combination should exist, and this reversibility must be variable according to the condition, as is the case with adsorption phenomena in general. Reversibility can be demonstrated in the case of some antigen-antibody systems, a reversibility which is variable and generally incomplete. On the whole, almost every phenomenon of the toxin-antitoxin reaction seems to be explicable on Bordet's adsorption hypothesis, which is not the case with other hypotheses. Specificity is not completely explained by it, nor, however, is it explained by other hypotheses.

[On the toxin-antitoxin reaction, *see* Ehrlich, Deutsch. med. Woch. 1898; Arrhenius, Immuno-Chemistry (Macmillan Co., 1907), Ergebnisse der Physiol. vii. Jahr., 1908, and Jour. of Hygiene, viii.; Bordet, Ann. Inst. Pasteur. 1899, 1900, 1903; Craw, Jour. of Hygiene, vii., ix.; McKendrick, Proc. Roy. Soc. Lond. B. 1911; Gengou, Jour. State Med. 1912, xx. (Summary and full Bibliog.). Many abstracts in J. Chem. Soc.] R. T. H.

TOXICODENDROL. The active principle of the 'Poison Ivy' (*Rhus Toxicodendron* [Linn.] and *R. venenata* [DC.]), is an oily substance possessng intensely irritating properties, found in all parts of the plant, the fruits giving 3·6, the eaves 3·3, and the stem 1·6 p.c. The degree of activity varies in the case of different persons: in some cases 1 mgm. produced hundreds of vesicles, and even $\frac{1}{1000}$ mgm. proved active in one case. The vesicant action was not immediate, a period of 24 hours to 7 or 9 days elapsing before the eruption appeared (Pfaff, J. Soc. Chem. Ind. 1897, 1037).

The poisonous substance is probably a glucoside; it is decomposed by acids yielding gallic acid, fisetin, and rhamnose. Cases of poisoning are said to be best treated with potassium permanganate (Acree and Syme, Amer. Chem. J. 1906, 301).

TRAGACANTH. *Tragacanthin* v. GUMS.

TRAUMATOL v. SYNTHETIC DRUGS.

TRAVERTINE. A limestone deposited by calcareous springs, known also as *calc-sinter* and *calcareous tufa.* The typical travertine occurs near Tivoli, the ancient Tibur, whence the name *apis Tiburtinus.* The most important sources at this locality are the sulphuro-calcareous springs, known as the Acque Albule, surrounded by a plain representing the floor of an ancient ake, and consisting of thick beds of travertine. This stone, being easily worked and of great durability, and presenting a pleasing tone, has for ages been the favourite building material in Rome. The quarries of Barco, on the Anio, furnished the stone for the Coliseum, and those of Fosse the material for St. Peter's. To supply modern Rome new quarries have been opened at the Villa Adriana, below Tivoli (N. Pelati, I Travertini della Campagna Romana, Rome, 1882; P. Zezi, in Johnston-Lavis's South Italian Volcanoes, Naples, 1891).

Springs issuing from limestone rocks commonly precipitate calcium carbonate upon objects with which they come in contact, and are thus improperly termed 'petrifying springs.' Calcareous incrustations are formed, for instance, by water issuing from the carboniferous limestone at Matlock, in Derbyshire; whilst extensive accumulations of tufa are produced by the thermal springs of Clermont, in Auvergne, and of Hieropolis, in Asia Minor.

The deposition of travertine, or tufa, may result from the mere exposure of highly calcareous waters to atmospheric influences, carbon dioxide being removed and the normal calcium carbonate precipitated. Agitation of the water facilitates the loss of carbon dioxide, and hence calcareous deposits often occur where the water falls in a spray or cascade. Deposition is also favoured by the action of heat, by diminution of pressure, and by the agency of plants. It was shown by F. Cohn that in the hot springs of Carlsbad microscopic plants are important agents in determining the deposition of calcareous tufa, or *Sprudelstein.* F. W. R.

TREACLE v. SUGAR.

TREE WAX v. *Insect wax*, art. WAXES.

TREHALOSE v. CARBOHYDRATES.

TREMOLITE-ASBESTOS v. ASBESTOS.

TRENT SAND. A sand found in the Trent, Severn, and in other rivers; used for polishng.

TRIDECATOIC or **TRIDECYLIC ACID** $C_{12}H_{25}·COOH$ is obtained by the oxidation of methyl-tridecyl-ketone; it crystallises in thin plates; m.p. 40·5°; b.p. 236° (100 mm.) (Krafft, Ber. 1879, 1668).

TRIDYMITE v. QUARTZ.

TRIFOLIN v. GLUCOSIDES.

TRIGEMIN, TRIPHENIN, v. SYNTHETIC DRUGS.

TRIGONELLINE (*Methyl betaïne of nicotinic acid*) $C_7H_7NO_2$ is an alkaloid which occurs in the seeds of *Trigonella Foenum-graecum* (Linn.); in ordinary peas (*Pisum sativum* [Linn.]); in hemp seeds (*Cannibis sativa* [Linn.]) (Jahns, Ber. 1885, 18, 2518; Schulze and Frankfurt, *ibid.* 1894, 27, 769; Schulze and Winterstein, Landw. Versuchs. Stats. 1895, 46, 23); in commercial strophanthine and in the seeds of *Strophanthus hispidus* (DC.) and *S. Kombé* (Oliver) (Thoms, Ber. 1898, 31, 271, 404; Karsten, Chem. Zentr. 1902, ii. 1514).

Preparation. The powdered seeds are extracted with alcohol; after distilling off the latter, lead acetate and caustic soda are added, and the alkaloid is separated by means of potassium bismuth iodide and sulphuric acid. The precipitate is then treated with caustic soda to separate albuminoids, the filtered solution is neutralised with sulphuric acid and precipitated with mercuric chloride. The cholin so precipitated is removed by filteration, the filtrate acidified with sulphuric acid, and the trigonelline in the form of its mercury iodide salt is then precipitated. The free base is obtained by decomposing the double salt with a sulphide (*see* Schulze, Zeitsch. physiol. Chem. 1909, 60, 155).

Trigonelline has also been obtained by treating nicotinic acid with methyl iodide, and the product of the reaction with silver hydroxide (Hantzsch, Ber. 1886, 19, 31); or by the oxidation of nicotine *iso*-methohydroxide, with potassium permanganate (Pictet and Genequand, Ber. 1897, 30, 2117, 2122).

Trigonelline crystallises with one molecule of water, forming colourless, flat prisms of feeble saline taste and neutral reaction. It is hygroscopic, is readily soluble in water, sparingly soluble in alcohol, insoluble in ether, benzene, and chloroform. When heated, it loses its water of crystallisation and dissolves or melts in the latter at 130°. The anhydrous alkaloid darkens when heated at 200°, and melts at 218° (decomp.). When heated with barium hydroxide at 120° trigonelline evolves all its nitrogen as dimethylamine, and when heated with excess of hydrochloric acid, it yields nicotinic acid and a gas, probably methyl chloride (Jahns, Ber. 1887, 20, 2840). It gives the usual reactions of an alkaloid with reagents.

A *hydrochloride, platinochloride,* and two *aurochlorides* $C_7H_7NO_2·HCl·AuCl_3$, m.p. 198°, and $4(C_7H_7NO_2)3HCl·3AuCl_3$, m.p. 186° (Jahns, *l.c.*; Schulze and Frankfurt, *l.c.*), are known. For the physiological action of trigonelline, *see* Kohlrausch, Chem. Zentr. 1909, ii. 465; for its origin, *see* Schulze and Trier, Zeitsch. physiol. Chem. 1910, 67, 46) v. VEGETO-ALKALOIDS.

TRIHYDROXYBENZENE v. PHENOL AND ITS HOMOLOGUES.

TRIKETOHYDRINDENE v. INDENE.

TRIKETONES v. KETONES.

TRIMETHYLACETIC ACID v. VALERIC ACIDS.

TRIMETHYLBENZENES *v.* Cumenes.

TRIMETHYLENE *v.* Propyl.

TRIMETHYLHYDROXYBENZENE *v.* Phenol and its homologues.

TRINITROPHENOL *v.* Picric acid.

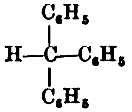
TRIONAL (*diethylsulphonemethylethylmethane* or *methyl sulphonal*) $CH_3(C_2H_5)C(SO_2C_2H_5)_2$ is prepared, like sulphonal and tetronal, from methylethylketone and ethyl mercaptan (Fromm, Annalen, 1889, 253, 150; D. R. P. 49073; Frdl. 1887–1890, ii. 521). It forms colourless, odourless, lustrous square tablets, m.p. 76°, soluble in 320 parts of cold water, but more readily so in boiling water, in ether, and in alcohol. It is employed in medicine for the same purposes as sulphonal and tetronal, *v.* Synthetic Drugs. For its detection, *v.* Sulphonal and Tetronal.

TRIPHANE *v.* Spodumene.

TRIPHENYLMETHANE COLOURING MATTERS. This is the generic name of a very large and varied class of artificial dye-stuffs which have been obtained by very different methods. Some of the oldest artificial dye-stuffs belong to this group. Their generic connection was, in many instances, not known until their constitution was fully ascertained. When this had been done, a large number of new dye-stuffs belonging to the same class was prepared by direct synthesis. The members of this group vary more than those of any other in their physical properties; they represent almost every possible shade, and include dye-stuffs suitable for almost every kind of dyeing and printing process. They are applicable to silk, wool, and cotton dyeing; as a rule, they are of very pure and brilliant shades—in fact, the most brilliant of all colouring matters are found amongst them. Many are rather fugitive, especially the older ones—magenta-red and its congeners. It is for this reason that aniline dyes generally have been declared fugitive and unstable by people of hasty judgment. This want of stability is, however, not characteristic of the triphenylmethane group; some of the best and most permanent dye-stuffs belong to it. It may be well to remark at once that resistance to light and other influences seems not to be directly related to the chemical constitution of these substances, as it is frequently observed that of two dye-stuffs of very similar constitution one may be very fugitive, whilst the other is remarkable for its fastness. The fastness of these and other dye-stuffs also depends to some extent on the manner in which they are applied to the textile fibre.

The members of this family are not, like those of the azo- group, connected by one generic method, by which all of them might be produced from various materials. Nor is it possible to enumerate a number of general synthetic methods which result in their production. The methods applicable are so numerous that no generalisation is possible. The only connecting link between all these dyes is their chemical constitution, which is now well established in almost every case; it is also in this constitution that we find the necessary criteria for the subdivision of the group. Some introductory remarks about the constitution of these dyes are therefore necessary for a complete revision of the subject.

If we consider the constitution of these colouring matters, we observe that there is but one characteristic feature common to them all. This is the presence of an atom of carbon connected by three of its valencies to three aromatic radicles. The compound of the simplest constitutional formula in which this 'central carbon' (as we will henceforth call it) is observed is the hydrocarbon triphenylmethane, the formula of which is $C_{19}H_{16}$:

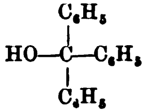


$$H-\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{C}}-C_6H_5$$

Triphenylmethane thus becomes the prototype of all the members of this group; it is for this reason that the name of *triphenylmethane colouring matters* was chosen.

Triphenylmethane was first prepared by Kekulé and Franchimont, in 1872, by heating benzylidene chloride with mercury diphenide to 150° (Ber. 5, 907). Its formation has since been observed in numerous reactions. The best method for preparing it consists in treating a mixture of two parts of chloroform and seven parts of benzene with aluminium chloride, until no more hydrogen chloride is given off. The resulting liquid is washed with water and dried. On distillation it yields benzene, diphenylmethane, and triphenylmethane. The last may be purified by crystallisation. This method was indicated by Friedel and Crafts (Ann. Chim. Phys. [vi.] 1, 489). Triphenylmethane is obtained in colourless crystals; m.p. 92°; b.p. 358°–359°. It is capable of forming a molecular compound with benzene. Of its derivatives the following three are important on account of their relations to the colouring matters under consideration.

Triphenyl carbinol $C_{19}H_{16}O$ is the tertiary alcohol derived from triphenylmethane:

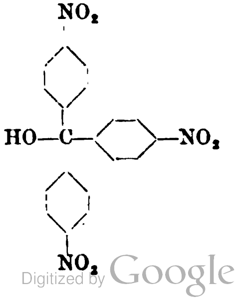


$$HO-\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{C}}-C_6H_5$$

It is easily obtained by oxidising the hydrocarbon by means of chromic acid. It forms colourless crystals, melting at 159° and boiling at 360° (E. and O. Fischer, Annalen, 194, 274).

Trinitrotriphenylmethane $C_{19}H_{13}N_3O_6$ is obtained by treating the hydrocarbon with strong nitric acid. Crystals, melting at 203°. Chromic acid transforms it into trinitrotriphenylcarbinol (E. and O. Fischer, *ibid.* 194, 256).

Tri-*p*-nitrotriphenylcarbinol $C_{19}H_{13}N_3O_7$:

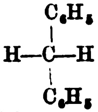


is best crystallised from glacial acetic acid and forms small crystals, melting at 171°–172° and soluble in alcoholic potash solution with a beautiful reddish-blue colour.

None of the above substances is a colouring matter, nor are they even coloured. But if we reduce trinitrotriphenylcarbinol by adding zinc-dust to its solution in acetic acid, we obtain triaminotriphenylcarbinol, which is identical with pararosaniline. By showing this identity, E. and O. Fischer solved the problem of the constitution of this very important colouring matter. Leucaniline, the reduction product of rosaniline, was shown to be identical with triaminotriphenylmethane. This discovery became the starting-point for very important theoretical and practical work. All the congeners of rosaniline were shown to be derivatives of triphenylmethane or analogous hydrocarbons, and new synthetical methods were devised by which such derivatives could be obtained.

It is quite obvious that not only triphenylmethane, but also all its homologues and analogous hydrocarbons, are parent substances of dye-stuffs. The number of such hydrocarbons indicated by theory is very large, since every one of the three phenyl radicles connected with the central carbon may be replaced by any other aromatic radicle. Every one of the hydrocarbons thus formed is capable of yielding, like triphenylmethane itself, a very large number of colouring matters, as will be seen from subsequent considerations. It thus becomes evident that the theoretical number of possible triphenylmethane colouring matters is almost unlimited. It has, however, been shown that the variation of the aromatic radicles connected with the central carbon is not the only point of importance as regards the variation of the shades and properties of the resulting dye-stuffs. The triphenylmethane colouring matters in actual use are the derivatives of a very few hydrocarbons, of which triphenylmethane itself is by far the most important. Tolyldiphenylmethane, ditolylphenylmethane, tritolylmethane, and naphthyldiphenylmethane are the principal parent substances of a large number of colouring matters, which at present form the object of regular and extensive manufacture, and of several hundred more which have been prepared and patented without coming into general use. The extensive range of shade and general applicability, so characteristic of the colouring matters of this class, and unequalled by any other class of dye-stuffs known, is not so much a result of the variation of the hydrocarbons forming their parent substances, as of the extremely large number of coloured derivatives which may be produced from every one of these hydrocarbons. No other branch of the chemistry of dye-stuffs is so extremely fertile in the synthetical methods at its disposal as this, and every one of these methods forms an easy way for the production of a considerable number of dye-stuffs, which can generally be produced by this one method alone. Many of these methods, both empirical and synthetical, have been patented, and some of these patents are of great value and importance. They are generally "process" patents, claiming new methods of manufacture; in this respect they form the exact counterpart of the still more numerous "substance" patents for azo- colouring matters, which, being all based on the same method of work, only claim the novelty of the product obtained by varying the ingredients of the process.

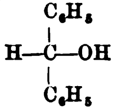
Before entering into the details of the constitution of triphenylmethane dye-stuffs, and the connection of this constitution with the properties of the dyes, we have to describe another substance closely related to triphenylmethane, some of the derivatives of which are dye-stuffs similar to those derived from triphenylmethane itself, whilst others play an important part in the processes for the production of triphenylmethane colouring matters. This substance is also a hydrocarbon, derived from methane by replacing only two of its hydrogen atoms by the aromatic radicle phenyl. This hydrocarbon is *diphenylmethane*, or benzyl-benzene $C_{13}H_{12}$:



$$\begin{array}{c} C_6H_5 \\ | \\ H—C—H \\ | \\ C_6H_5 \end{array}$$

It was discovered by Zincke in 1873 (Annalen, 159, 374), and is best prepared by the method indicated by Friedel and Balsohn (Bull. Soc. chim. [ii.] 33, 337), by adding aluminium chloride to a mixture of 1 part benzyl chloride with 5 parts of benzene. It melts at 26°–27°, and boils at 261°–262°. It forms white crystals, possessing an agreeable odour of oranges. Of its derivatives the following are of practical importance:—

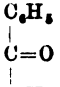
Diphenylcarbinol or **benzhydrol** $C_{13}H_{12}O$ is the corresponding alcohol:



$$\begin{array}{c} C_6H_5 \\ | \\ H—C—OH \\ | \\ C_6H_5 \end{array}$$

It is prepared by boiling benzophenone with alcoholic potash solution and zinc-dust. It forms white crystals, melting at 67·5°–68°, boiling at 297°–298° (Linnemann, Annalen, 133, 6; Zagumenny, *ibid.* 184, 174).

Benzophenone $C_{13}H_{10}O$ is the second product of oxidation of diphenylmethane, to which it stands in the same relation as that which exists between propane and acetone. Benzophenone is the typical ketone of the aromatic series



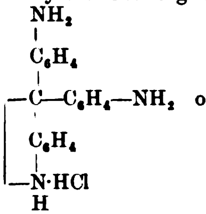
$$\begin{array}{c} C_6H_5 \\ | \\ C=O \\ | \\ C_6H_5 \end{array}$$

It is prepared by the process which led to its original discovery, by distilling calcium benzoate, or, better still, by distilling a mixture of calcium and zinc benzoate. Another process consists in adding aluminium chloride to a solution of carbonyl chloride $COCl_2$ (phosgene) in pure benzene, or to a mixture of benzene with benzoyl chloride. Benzophenone forms beautiful prismatic crystals, melting at 48°–48·5°, distilling at 305° (Péligot, Annalen, 12, 41; Chancel, *ibid.* 72, 279; Friedel, Crafts and Ador, Ber. 10, 1854) (*v.* QUINONES).

The amino derivatives of diphenylmethane, diphenylcarbinol, and benzophenone, which are of special importance in the chemistry of the triphenylmethane dye-stuffs, will be described subsequently in connection with the dye-stuffs to which they give rise.

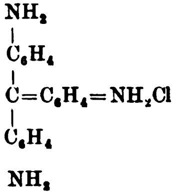
The substances mentioned so far, although the parent substances of so many beautiful dyes, are all perfectly colourless. Even triaminotriphenylcarbinol, which is identical with *p*-rosaniline, is perfectly colourless; it only becomes a dye-stuff by being dissolved in an acid, a reaction from which one might infer that *p*-fuchsin, the typical magenta colour, is merely a salt of *p*-rosaniline. This is, however, not the case, although colour-makers are apt to call, for simplicity's sake, the rosanilines 'magenta bases.' The dissolution of any or either of the aminocarbinols in an acid is invariably accompanied by a condensation in the molecule, and a loss of one molecule of water. The basic triphenylmethane colouring matters are therefore free from oxygen (unless they contain it in the shape of water of crystallisation); if we decompose the salts, by the addition of an alkali, coloured bases are formed, which, however, are very unstable. They take up, at once, one molecule of water, and re-form the original colourless or faintly-coloured carbinol base. If the precipitation is carried out by means of ammonia instead of sodium hydroxide or carbonate, or if ammonia be present in the liquid, the carbinol base is partly or wholly transformed into the corresponding amino compound, as has been shown by Villiger and Kopetschni, Ber. 45, 2910, and by Nölting and Saas, *ibid.* 46, 952. By this observation it is clearly shown that something more than the presence of the 'central carbon' is necessary for the formation of a triphenylmethane colouring matter. We have, therefore, to consider the constitution of the colouring matters themselves to obtain a knowledge of the chromophoric group of these dye-stuffs. This consideration leads at the same time to an easy and useful classification, to a subdivision into a series of smaller groups, the members of which show a closer connection in their methods of formation, their physical properties, and their manner of application.

The constitution of parafuchsin is now established beyond any doubt. It may be represented by the following formulæ:



$$\begin{array}{l} NH_2 \\ | \\ C_6H_4 \\ | \\ -C-C_6H_4-NH_2 \\ | \\ C_6H_4 \\ | \\ -N{\cdot}HCl \\ H \end{array}$$

or



$$\begin{array}{l} NH_2 \\ | \\ C_6H_4 \\ | \\ C=C_6H_4=NH_2Cl \\ | \\ C_6H_4 \\ NH_2 \end{array}$$

I. II.

which are practically identical, II. corresponding to the modern way of expressing 'quinonoid' structure. This formulation will therefore be used exclusively in this article to explain the constitution of the dyestuffs to which it refers, whilst formulæ corresponding to I. have been used in the first edition of this work. The formulæ chosen show also the typical constitution of all the congeners of magenta, every one of which may be represented by similar formulæ, in which either one or more of the phenyl radicles is replaced by other aromatic radicles, or one of the amino groups replaced by hydrogen, or one of the six available hydrogen atoms of the amino groups replaced by radicles of the fatty or aromatic series, or several of these changes introduced at the same time. It will at once be obvious that several thousand different combinations may thus be produced, all colouring matters of different shades, but showing in their properties a general resemblance to parafuchsin. The constitutional formulæ of all these colouring matters have but one thing in common besides the 'central carbon' (which is, as has been said, characteristic not only of these, but also of all the other triphenylmethane colouring matters); this one essential feature is the quinonoid nature of the substance, expressed in the structural formula either by the connection between the central carbon atom and the pentavalent nitrogen (as shown in formula I.), or, as it has become customary of late, by shifting the double valencies in the benzene hexagon and connecting it accordingly with the other parts of the molecule, as shown in formula II. We have, therefore, a perfect right to claim this invariably present quinonoid configuration as the essential feature of the whole molecule, and as the cause of its being a colouring matter. It forms a part of the chromophoric group of the fuchsin family.

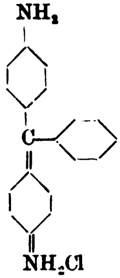
It is, however, important to notice that, no matter how we write the structural formula of *p*-fuchsin or any of its congeners, whether we use the older or the more modern way of expressing the quinonoid nature of the substance, one of the amino groups present is always taking part in the quinonoid chromophoric group and therefore is no longer available as an auxochromic group. To supply this, at least one more amino-group must be present, and this is the reason why only di- or poly-amino derivatives of triphenylmethane can become mother-substances of dye-stuffs belonging to this group. On the other hand, both the amino groups of auxochromic nature, as well as the one entering into the chromophoric part of the molecule, may be replaced by other suitable groups. The hydroxyl group with its tendency to form salts by combining with metallic ions is as important an auxochromic group in the series of triphenylmethane dye-stuffs as in any other. And the quinonoid imino group contained in the chromophore, may, as in other dye-stuffs, be replaced by an oxygen atom acting in similar capacity. Thus we obtain two separate groups of dye-stuffs, the first of which, generally called the *fuchsin group*, is characterised by the presence of nitrogen and the basic nature of its members; the second, called the *aurin group*, by the absence of nitrogen and the phenolic character of the dyestuffs it embraces. In addition to these two groups, a third one, the *phthalein group*, has been established by the common consent of all authors on the subject. This group contains a large number of important dye-stuffs of both basic and acid nature, which have this in common, that they are all derived from phthalic acid and take their 'central carbon' from one of the carboxyl groups of this acid, whilst the other, remaining available, enters the molecule of the dye-stuff and thus renders the latter a true organic acid, which is not necessarily the case amongst the members of the fuchsin and aurin group. Moreover, almost all the phthalein dye-stuffs of any practical importance contain, in addition to the typical chromophor of the triphenylmethane colouring matters, an additional one in the shape of the 'pyrone' ring, formed by the elimination of water from certain suitably placed hydroxyl groups of the molecule. This pyrone ring will be easily recognised in the formulæ of the members of the phthalein group to be given subsequently. The fact that only those phthaleins, which contain this pyrone ring, are colouring matters of any practical value, greatly diminishes the number of possibilities for the synthesis of such dye-stuffs, which might be made to form a class of their own, if it had not become customary to treat them as a special division of the triphenylmethane group of colouring-matters.

We now proceed to give a detailed account of these three groups and their various members, of which, however, we shall enumerate only those which are, either scientifically or practically, important. For a complete list we refer the reader to the well-known tables of Schultz and Julius.[1]

I. The Fuchsin Group.

(A) *Diaminotriphenylmethane derivatives.* The simplest type of these colouring matters is

1. **Benzaldehyde violet** $C_{19}H_{17}N_2Cl$ or

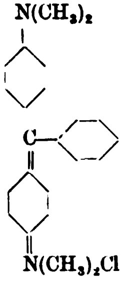


which may be prepared from diaminotriphenylmethane by oxidation. The yields are, however, very poor, and the colour itself is of no great value. Its manufacture has, therefore, never been taken up.

The derivatives of this substance, however, in which the hydrogen of its two amino groups is replaced by various radicles of either the fatty or aromatic series, are of great value and importance. Of these, the oldest, best known, and simplest in its constitution, is

2. **Benzaldehyde green.** (Syn. *Malachite green, New green, Victoria green, Fast green, Diamond green, Benzoyl green, Benzal green.*)

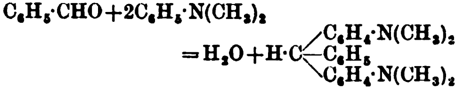
$C_{23}H_{25}N_2Cl$ or



This product was discovered almost simultaneously by Otto Fischer (1877; Ber. 10, 1625) and O. Döbner (1878; *ibid.* 11, 1236), who prepared it by different methods. For some time it was believed that Döbner's product was different from Fischer's until their identity was finally established. Döbner's process was patented (D. R. P. 4322). Fischer's process found, however, more favour with the majority of manufacturers, and has mostly been adopted.

Fischer's process gave bad yields and a poor product at first, until the best method for its manufacture was worked out. It consists in the following operations:—

(*a*) Manufacture of tetramethyldiaminotriphenylmethane by the action of benzaldehyde on dimethylaniline:



$$C_6H_5{\cdot}CHO + 2C_6H_5{\cdot}N(CH_3)_2 = H_2O + H{\cdot}C\begin{cases}C_6H_4{\cdot}N(CH_3)_2\\C_6H_5\\C_6H_4{\cdot}N(CH_3)_2\end{cases}$$

The base obtained in this reaction is generally called 'green leuco base' by the manufacturers. For preparing it one molecule of benzaldehyde is mixed with very little more than two molecules of absolutely pure dimethylaniline, a substance capable of absorbing the water formed in the reaction being added. Dry zinc chloride was originally employed, and is still used by many manufacturers. In quantity it should be equal in weight to the aldehyde employed. Hydrochloric, sulphuric, or anhydrous oxalic acid, or acid sodium sulphate may be used instead of the zinc salt. The mixture is heated in a jacketed still to 100°–110° for about forty-five to forty-eight hours. The product is then transferred to a still, a sufficient quantity of caustic soda is added to make the mixture alkaline to test-paper, and a current of steam is blown through the liquid in order to remove every trace of dimethylaniline and benzaldehyde. The leuco base is not volatile; it remains in the still in the shape of a viscid mass, which solidifies into white crystals after a while. This base is now subjected to the second operation.

(*b*) Oxidation into green. It is here that great difficulties were encountered in the beginning of the manufacture. Special conditions are required to obtain a good crystallisable dye-stuff. If these are not strictly adhered to, a non-crystallisable green is the result. The latter is different from the crystallisable substance in composition, containing one methyl group less, which is lost in the shape of formaldehyde by a too powerful action of the oxidising agents. The following conditions give excellent results: 33 kilos of leuco base are dissolved in 25 kilos of ordinary hydrochloric acid, and diluted with 200 litres of water; 30 kilos of ordinary acetic acid of 45–50 p.c. are then added. It is necessary that these two acids should be present; neither of them can be replaced by another acid of equal strength. The solution is then oxidised in the cold (in the summer it is advisable to add some ice) with a paste of lead peroxide of known strength. The peroxide should be tested by the oxalic acid method (determination of the CO_2 evolved from an excess of oxalic acid by the peroxide in question), and not by the iodometric method, as the latter gives too high results. Every kind of lead peroxide contains a certain amount o

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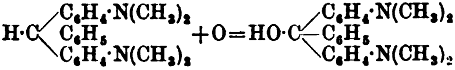
[1] *Gustav Schultz und Paul Julius.* Tabellarische Uebersicht der künstlichen organischen Farbstoffe. Vierte Auflage, Berlin, 1902. (Fifth edition now in progress.)

crystalline peroxide, which neither acts on the leuco base, and is therefore quite irrelevant in its oxidation into green, nor on oxalic acid, whilst the iodometric method gives values for both modifications indiscriminately. For oxidising the leuco base the exact quantity of peroxide should be taken, which is indicated by the following equation:

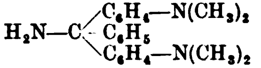


$$H\cdot C\begin{cases}C_6H_4\cdot N(CH_3)_2\\ C_6H_5\\ C_6H_4\cdot N(CH_3)_2\end{cases}+O=HO\cdot C\begin{cases}C_6H_4\cdot N(CH_3)_2\\ C_6H_5\\ C_6H_4\cdot N(CH_3)_2\end{cases}$$

One molecule of active peroxide is, therefore, required for every molecule of the base.

As soon as the peroxide has been added with constant stirring, the liquid turns a deep green. From this liquid the dye-stuff may be separated by various methods; an addition of zinc chloride solution is generally recommended. This, however, precipitates both the crystalline green and the tarry modification which is never quite absent. The following process has given excellent results in the hands of the writer.

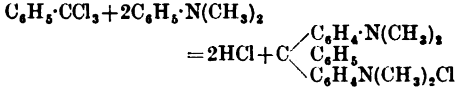
The green liquid obtained by oxidation is saturated with common salt. On standing small glittering scales of the lead double chloride of the crystallisable green very soon make their appearance, and are collected on a filter. From the mother-liquor an inferior quality of green may be obtained by adding a solution of sodium sulphate, filtering, and precipitating with zinc chloride and common salt. The crystals of the lead double chloride are dissolved in hot water, and sufficient sodium sulphate is added to precipitate the lead. The liquid is then filtered and precipitated with ammonia. The 'green base' (a mixture of tetramethyl-diaminotriphenyl carbinol with the corresponding amino derivative



$$H_2N-C\begin{cases}C_6H_4-N(CH_3)_2\\ C_6H_5\\ C_6H_4-N(CH_3)_2\end{cases}$$

discovered by Villiger and Kopetschni) settles out in the shape of a pink precipitate, which is filtered off and washed. From it the 'green crystals' of commerce may be prepared, either by dissolving it in a hot solution of oxalic acid and allowing the liquid to cool very slowly, or by dissolving it in dilute hydrochloric acid and adding a solution of zinc chloride. Besides these two the iron double salt is also occasionally met with in commerce. The picrate is also sold under the name of 'spirit green.'

Döbner's process. This consists in heating dimethylaniline with benzotrichloride in presence of metallic chlorides. This process has certain advantages if benzotrichloride is available at a low price. It may be represented by the following equation:



$$C_6H_5\cdot CCl_3+2C_6H_5\cdot N(CH_3)_2$$
$$=2HCl+C\begin{cases}C_6H_4\cdot N(CH_3)_2\\ C_6H_5\\ C_6H_4N(CH_3)_2Cl\end{cases}$$

The following proportions are recommended in the patent:

3 parts dimethylaniline,
2 „ benzotrichloride,
1·5 „ zinc chloride,

These are to be heated for three hours to 110° in an enamelled iron vessel with constant stirring. The resulting melt is transferred to a still, and steam is blown through it to remove all excess of trichloride. It is then thoroughly extracted by boiling water. The filtrate is now precipitated by salt, and the precipitate recrystallised from water. The dye-stuff is always obtained in the shape of the zinc double chloride.

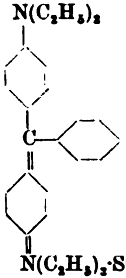
The oxalate of benzaldehyde green forms large plates of an intense grass-green colour, which dissolve easily in hot water. It contains three molecules of oxalic acid to every two of green base.

The zinc double chloride, which has the composition $3(C_{22}H_{25}N_2Cl),2ZnCl_2,2H_2O$, forms green crystals with a fine yellow metallic lustre. It is not quite so easily soluble as the oxalate.

The application of these salts is similar to that of all the basic dye-stuffs, and need not here be described.

3. **Brilliant green.** (Syn., *Ethyl green*, *Emerald green*; also all the other names given for the preceding compound, with the addition of the letters G, J, or Y (meaning *gelb*, *jaune*, or *yellow*).

$C_{27}H_{34}N_2O_4S$:



is prepared from diethylaniline by exactly the same process as described for benzaldehyde green. After precipitating the free green base, it is transformed into its sulphate by mixing it with the theoretical quantity of sulphuric acid diluted with its own weight of alcohol. The mixture forms a thick tar at first, but suddenly solidifies into a mass of well-defined crystals.

The shade of this green is considerably yellower than that of the ordinary benzaldehyde green.

4. **Victoria green** 3 B, $C_{23}H_{22}N_2Cl_2$. This is a colouring matter prepared from dichlorobenzaldehyde instead of the ordinary benzaldehyde. It is considerably bluer in shade than the ordinary benzaldehyde green. A large number of similarly constituted bluish-greens and greenish-blues is manufactured and sold, especially by the Swiss colour-works.

Acid greens. Considerable importance has always been attached by dyers to the sulpho derivatives of basic colouring matters, because these are more easily and evenly dyed on wool than the hydrochlorides and other salts of the bases themselves. Many attempts have, therefore, been made to obtain acid greens. They were at first only partly successful; at present there are, however, several acid greens in commerce, ranging in shade from a yellowish green to a clear greenish indigo blue. They are very largely used in wool dyeing, especially for mixed shades.

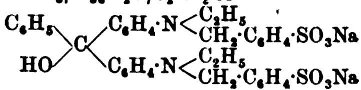
The oldest of these acid greens, which appeared in the market in 1878, was called

5. **Helvetia green** or **Acid green C.** It was the sodium sulphate of the mono-sulpho derivative of

the ordinary benzaldehyde green, prepared either by sulphonating the green itself by means of chlorosulphonic acid, or by sulphonating tetramethyldiaminotriphenylmethane and oxidising the resulting colourless acid by means of lead peroxide. Neither of these two methods works satisfactorily. For this reason the product has gradually been abandoned, and replaced by the benzyl derivatives, which are more easily prepared, and at the same time much more brilliant in shade.

6. **Benzyl acid greens.** In the various attempts to prepare acid greens it was found that the phenyl groups, combined with the central carbon, show little tendency to permit of the introduction of the sulpho group. This reluctance is, indeed, quite characteristic of all triphenylmethane derivatives. It is the cause of the difficulties experienced in preparing sulphonated derivatives of these dye-stuffs. It was, therefore, a happy thought to introduce into the molecule of the green an independent radicle, capable of receiving the sulpho group without influencing more than necessary the shade and other properties of the green. Such a radicle was found in the benzyl group. If we introduce this, instead of methyl and ethyl, into the amino groups of the green, it acts in the manner of a radicle of the fatty series, influencing the shade of the green very little. The C_6H_5 group, however, brought into the molecule as a constituent of the benzyl radicle, is capable of being sulphonated with the greatest facility. Various dye-stuffs have been prepared according to this principle. Of these *Guinea green B* is the simplest. It is the disulpho derivative of diethyl dibenzyldiaminotriphenyl carbinol

$C_{37}H_{36}N_2O_7S_2Na_2$ or



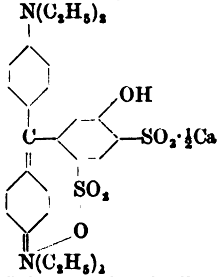
$$\begin{array}{l} C_6H_5 \\ HO \end{array} \!\!>\! C \!<\! \begin{array}{l} C_6H_4 \cdot N \!<\! \begin{array}{l} C_2H_5 \\ CH_2 \cdot C_6H_4 \cdot SO_3Na \end{array} \\ C_6H_4 \cdot N \!<\! \begin{array}{l} C_2H_5 \\ CH_2 \cdot C_6H_4 \cdot SO_3Na \end{array} \end{array}$$

obtained by combining benzaldehyde with two molecules of ethylbenzylaniline sulphonic acid, and oxidising the leuco compound thus obtained. This product was discovered by G. Schultz and Streng, in 1883, and patented (D. R. P. 50782, 1889; Eng. Pat. 7550, 1889). It is an excellent and very useful dye-stuff. *Guinea green B V*, which dyes a more yellowish shade, is obtained in the same manner, using *m*-nitrobenzaldehyde instead of the ordinary benzaldehyde.

The various shades of *light green* or *acid green* sold by the majority of manufacturers are prepared somewhat differently. Benzaldehyde is combined with two molecules of benzyl-methyl or benzyl-ethylaniline. The base thus obtained is treated with sulphuric acid, when *three* sulpho groups enter the molecule, one of which is linked to the phenyl radicle containing no amino group, whilst the two others are combined with the benzyl radicles. The resulting trisulpho derivatives are oxidised in the usual manner, yielding the dye-stuffs in the shape of a very soluble green powder.

7. A curious product, belonging to the class of acid greens, was described by R. Meldola, under the name of *Viridin* (Chem. Soc. Trans. 1882, 187; Ber. 14, 1385). It was prepared by oxidising benzyl diphenylamine, and sulphonating the resulting green, dissolved in spirit. This green, or a substance very similar to it, had already been prepared by Ch. Girard (Wurtz, Progrès de l'Ind. des Mat. col.; Paris, 1876: p. 134).

8. **Patentblau, Patent blue**, a product of the Farbwerke vorm. Meister, Lucius und Brüning, in Höchst-am-Main. This is a dye-stuff closely allied to the acid greens. It was discovered by Hermann, and patented by the Farbwerke (D. R. P. 46384, 1888, and many additional patents). It is prepared by a somewhat complicated method. *m*-Nitrobenzaldehyde is combined with two molecules of dimethylaniline. The resulting base is reduced, the amino derivative diazotised, and, by boiling with water, transformed into *m*-hydroxytetramethyldiaminotriphenylmethane. This is sulphonated by treatment with sulphuric acid. The resulting sulpho derivative is oxidised and transformed into a calcium salt, which is delivered into the market. The constitution of the dye-stuff is represented by the following formula:

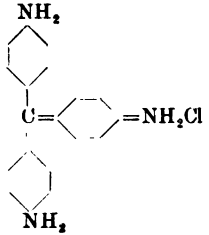


This dye-stuff dyes wool and silk a beautiful greenish-blue of great brilliancy and clearness. Several other dye-stuffs of very similar composition are on the market.

(B) *Derivatives of triaminotriphenylmethane.* This group contains some of the oldest artificial dye-stuffs, which were prepared by strictly empirical methods. When the constitution of the triphenylmethane group was established, synthetical methods for producing dye-stuffs of this group were gradually introduced. At the present time the old empirical processes hold their own for the production of the old colouring matters, whilst the synthetical methods, which are mostly patented, are used for preparing new dye-stuffs of great beauty and perfection.

The prototype of this group is—

1. **Parafuchsin**, *Paramagenta*, the anhydrochloride of triaminotriphenylcarbinol $C_{19}H_{18}N_3Cl$ the constitution of which is:



It always crystallises with four molecules of water of crystallisation, which should be added to the above formula.

This is the dye-stuff which was used by O. and E. Fischer for the elucidation of the chemistry of this class of substances (O. and E. Fischer, Annalen, 1878, 194, 242; Ber. 11, 1079; 13, 2204). It is one of the oldest artificial dye-stuffs; it was discovered in 1858 by A. W. Hofmann (J. 1858, 351); and re-discovered by Rosenstiehl in 1869 (Bull. Soc. Ind. Mulhouse, 36, 264). For a long time it was considered a substance of merely theoretical interest, because its shade is almost identical with that of ordinary fuchsin or magenta (see under 2), which is much more easily prepared. At present, however, it is manufactured on a large scale, not as a dye-stuff for sale, but as a raw material for certain blues, which will be mentioned later on.

A large number of reactions have been observed and described which result in the formation of pararosaniline. Of these the following may be mentioned:

(*a*) Pure aniline heated with carbon tetrachloride yields parafuchsin. This method was used on a manufacturing scale by Monnet and Dury in Lyons.

(*b*) Pure aniline, heated with iodoform, gives a fair yield of parafuchsin hydriodide.

(*c*) Pure aniline, heated with *p*-nitrobenzyl chloride in the presence of iron filings or iron salts gives a good yield of parafuchsin. This method, or modifications of it, form the substance of Greiff's and Baum's patents (D. R. PP. 15120 and 19304 Greiff, and 14929 Baum).

(*d*) Pure aurin (rosolic acid), which will be described subsequently, yields parafuchsin if strong ammonia be allowed to act on it for a long time at a high temperature.

(*e*) It has been shown (*v.* introduction) that the reduction-product of parafuchsin is para-leuco-aniline, and that the latter is identical with triaminotriphenylmethane. The latter may easily be prepared from triphenylmethane by nitration and reduction, and by various other methods. Attempts have not been wanting to work out a method for the production of parafuchsin from synthetical leucaniline. No good method, however, has hitherto been discovered for this purpose, and all the patents based on this reaction have proved failures. It is very easy to produce a trace of fuchsin in a solution of leucaniline; but no method is known for finishing the reaction.

(*f*) Mixtures of pure aniline with pure *p*-toluidine yield parafuchsin if subjected to oxidation. This is the usual practical way for the production of parafuchsin. The oxidation may be effected either by arsenic acid or by nitrobenzene. Other oxidising agents—such as mercuric chloride, stannic chloride, &c.—produce the same result, but at a higher cost. The arsenic acid process (which will be described later on) was for some time almost exclusively used for the production of parafuchsin. The chemical reaction which takes place is very simple. Arsenic acid is reduced to arsenious acid. The oxygen which is thus obtained combines with hydrogen of the aromatic bases:

$$2C_6H_5\cdot NH_2+C_6H_4(CH_3)NH_2+3O$$
$$=2H_2O+C_{19}H_{18}N_3OH$$

Triaminotriphenyl carbinol

The methyl group of *p*-toluidine is used up for yielding the central carbon around which the other radicles are grouped.

(*g*) Diaminodiphenylurethane, mixed with aniline and heated with oxidising agents, yields parafuchsin. This synthesis forms the basis o a more modern manufacturing process.

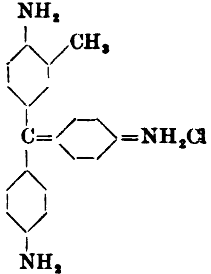
It has already been said that parafuchsi has no advantages over ordinary magenta re for dyeing purposes. It is, therefore, rarely t be met with as a dye-stuff in the market. As rule the melts are worked up in the same manne as ordinary magenta melts, but the resultin crystals of the pure hydrochloride are re dissolved and precipitated in the shape of para rosaniline base by the addition of soda or mil of lime. The base is then used for the production of blues.

Parafuchsin hydrochloride forms smal glistening crystals having a metallic gree lustre. As a rule, they are very small. muc smaller than the crystals of ordinary magenta Parafuchsin acetate is similar in appearance an crystallises much more easily than the ordinar magenta acetate.

Pararosaniline is important because it is th parent substance of all the various violets, an of some of the blues, which will be describe subsequently.

2. **Ordinary fuchsin, magenta red, rose** (*rubesine, harmaline, aniline red, azalein, solferino, erythrobenzine*) $C_{20}H_{20}N_3Cl$, is an articl of great importance and of very general application. The latter is due to the fact that it wa one of the first artificial dye-stuffs, although no one of the best. A great demand for it ha gradually been established, which forces th manufacturers to carry on its production on a large scale, even now, when much better dye-stuffs may be prepared by other methods.

Chemically, this colouring matter may b defined as the higher homologue of parafuchsin, in which one of the phenyl groups has been replaced by a tolyl group:



Ordinary fuchsin

The product of commerce, though chiefly composed of this substance, invariably contains an admixture of parafuchsin as wel as of the higher homologues $C_{21}H_{22}N_3Cl$ and $C_{22}H_{24}N_3Cl$. Like parafuchsin, it contains four molecules of water of crystallisation.

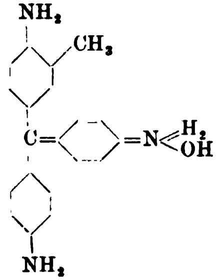
Fuchsin is invariably prepared by oxidisin a mixture of aniline with *p*-toluidine an *o*-toluidine. This mixture is generally known as 'aniline for red,' and was originally produced by the nitration and subsequent reduction of a certain fraction of crude benzene, which consisted of benzene and toluene. Sometime it even contained some xylene; in this ca xylidine entered into the composition of 'anilin for red.' At present most of the 'aniline fo red' is a mixture of pure aniline with crud toluidine. By the latter we mean the mixtur of *o*- and *p*-toluidine which is obtaine by the nitration and subsequent reduction of pure toluene. Crude toluidine consists as a rule of 55 p.c. *o*-toluidine and 45 p.c. *p*-toluidine. The quantity of aniline added to crude toluidine in order to produce the 'aniline oil for red' varies according to the recipes of various manufacturers. As a rule, half of the weight of the toluidine is added. A certain boiling-point (for instance, 188°–200°) and a certain specific gravity (for instance 1·010) are prescribed, and should be strictly adhered to by the aniline oil manufacturer. In some cases an addition of xylidine is necessary in order to produce a product of the desired boiling-point and density. Theoretically, an oil containing equal molecules of the three bases would be required; but for practical work an excess of aniline and *o*-toluidine is used, because a part of these two compounds escapes the reaction, whilst the *p*-toluidine is entirely used up.

Of all the methods which in the course of time have been proposed for oxidising this mixture, only two have survived, one of which is also rapidly disappearing. They are known under the names of the *arsenic acid melt* and the *nitrobenzene process*. From a practical point of view they are of equal value, but the arsenic acid melt is being abandoned on account of the poisonous nature of the arsenic compounds required.

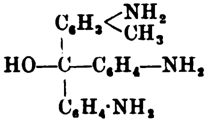
Magenta was originally prepared by Natanson, in 1856, by heating aniline with ethylene chloride. In 1858 Hofmann observed its formation when allowing carbon tetrachloride to act on aniline. In 1859 Verguin prepared it by the action of stannic chloride on aniline. Verguin's employers, the dyers Renard Frères and Franc, in Lyons, took up its manufacture on a large scale, and invented the name *fuchsin*. Later on a company was formed, under the name of 'La Fuchsin,' for working Verguin's patent. Gerber-Keller invented a process for oxidising aniline by means of mercuric nitrate. The dye-stuff thus obtained was believed to be different from fuchsin, and received the name *azalein*. In 1860 Medlock invented the arsenic acid process, which for a long time was considered the only practical method of manufacturing magenta. His patent was invalidated owing to a clerical error contained in the description. In 1869 Coupier described his process for producing fuchsin by the nitrobenzene process. This method, which did not give good results at first, was gradually worked out by various manufacturers, and is now equivalent, if not superior, to the best forms of the arsenic acid process.

Various salts of rosaniline were formerly in commerce. The original fuchsin was the hydrochloride, azalein was the nitrate; whilst magenta and rosein were the names applied to the acetate, produced by Nicholson, the first to manufacture this colouring matter in a practical and rational manner. Gradually the nitrate and acetate disappeared from the market. At present the hydrochloride is the only salt produced, to which, therefore, the original name of fuchsin should be applied. English manufacturers still use the names magenta and rosein for the hydrochloride. A large quantity of the fuchsin manufactured is transformed into rosaniline, which is delivered into the market either under this name or as 'magenta base,' 'red base,' or 'rosein base.' These names are not quite correct, because rosaniline may not strictly be considered as the true base of the hydrochloride of fuchsin.

The true base of fuchsin is



which, in the moment of its formation, undergoes a molecular transformation into



$$\begin{array}{c} C_6H_3{<}^{NH_2}_{CH_3} \\ | \\ HO{-}C{-}C_6H_4{-}NH_2 \\ | \\ C_6H_4{\cdot}NH_2 \end{array}$$

Rosaniline
(Triaminodiphenyltolylcarbinol)

Manufacture of Fuchsin.

1. *Arsenic acid process.* The properties of the 'aniline oil for red' have already been discussed. The mixture of bases known under this name is transformed into the dye-stuff by heating it with arsenic acid. The latter is prepared by oxidising arsenious acid (white arsenic) by means of nitric acid in closed earthenware pots. The escaping nitrous fumes are condensed in a tower, in which they meet an opposing current of water and air. The nitric acid is thus regenerated, and may be used again. Practically, therefore, the formation of the arsenic acid is accomplished by the oxygen of the air. The arsenic acid solution obtained has a sp.gr. of 1·85–2·3, and contains from 60–75 p.c. of arsenic acid H_3AsO_4. 1,500–1,700 kilos of this solution are required in order to oxidise 1,000 kilos of 'aniline oil for red.' These quantities of the reagents are introduced into enamelled cast-iron pots, closed by lids; a mechanical stirrer and a tube for the escape of the vapours should be provided. The mixture is then gradually heated to 180°. This temperature should be strictly maintained during the whole operation. If the temperature rise above 190°, the dye-stuff already formed is decomposed. From eight to ten hours are required in order to complete the reaction. During the whole time vapours escape, which should be condensed in a leaden coil connected with the escape tube, and cooled by a current of water. At first the distillate consists chiefly of the water introduced with the arsenic acid. Later on, the water formed in the reaction distils; at the same time some aniline oil goes over. The total quantity of the aniline escaping the reaction is one-third, or even one-half, of the quantity originally used. The melt, which is very thin at first, gradually becomes viscid; at the same time it assumes a brown, metallic lustre. Samples should be taken from time to time. When the melt becomes brittle on cooling, the reaction is finished, and the fire

should be drawn. The melt is then at once removed from the pot. In some factories an opening is provided for this purpose in the lowest part of the pot, which is closed by a lid and screw whilst the heating lasts. As a rule, however, it is preferred to remove the cover of the pot, and to ladle out the melt. The latter is spread on trays made of sheet iron. On cooling, it solidifies into cakes, which are very brittle, and break up into small lumps on being handled.

The crude melt contains the colouring matter in the shape of arsenite, together with an excess of arsenious and arsenic acids, some coloured by-products (*v. infra*), and a large quantity of tarry impurities. In order to obtain the pure dye-stuff, the crude melt is introduced into horizontal wrought-iron boilers, in which an eccentric horizontal stirrer is made to rotate. Water is added, the lid of the boiler is closed, and steam is introduced at a pressure of from four to five atmospheres. After several hours' vigorous stirring, the greater part of the rosaniline arsenite has been dissolved by the water. The liquid is then forced through felt into iron tanks, where it is allowed to cool down to 50°. A sufficient quantity of salt is then added to precipitate the whole of the colouring matter. By the addition of the salt a mutual decomposition takes place. Sodium arsenite is formed, and remains in the liquid, whilst the colouring matter is precipitated in the shape of chloride. It settles out as a thick green tar of metallic lustre, which solidifies into a brittle substance on cooling. The supernatant aqueous liquid is then drawn off, the crude fuchsin is chipped out, and introduced into another extractor, similar to the one used for treating the melt. A very small quantity of soda ash or chalk (about ½ p.c. of the weight of the crude dye-stuff) is added, and a second extraction takes place. The liquid is again forced through felt into large wooden vats, in which some wooden boards are suspended. When the vats are filled, a small quantity of hydrochloric acid and clean butter-salt is added to each vat. In these vats the dye-stuff separates out, in the shape of fine glistening green crystals. The largest crystals are generally deposited near the surface of the liquid. When the crystallisation is finished, the mother-liquor is drawn off, and the crystals are collected and sorted according to their shape and size. The largest crystals are sold under the name of 'diamond fuchsin.'

By-products. The residues of the first boiling may be subjected to a second extraction; as a rule, some hydrochloric acid is added in this case. A deeply-coloured solution is thus obtained, from which an impure colouring matter may be precipitated by the addition of salt. This colouring matter is sold under various names (*magenta cake, cerise, grenadine, maroon*), and finds a ready market. It dyes a magenta colour, which is less brilliant than the shade obtained with the crystals. A third boiling is sometimes necessary. The colouring matter obtained from this is very impure. It is, therefore, dissolved in weak hydrochloric acid, and some zinc-dust is added, which reduces the magenta contained in the liquid. On precipitating with salt, a colouring matter of a brown shade is obtained, which is sold as 'Nangking,' or 'leather brown.' The black insoluble residue of the third boiling still contains some dark-blue colouring matters of the induline series, which are, however, not worth the trouble of extracting.

The mother-liquors from the crystals contain a yellow colouring matter of great fastness and purity. This substance, known under the name of *phosphine*, belongs to another group of dyestuffs, being a salt of diaminophenylacridine. For extracting it from these mother-liquors, the latter should be acidified with hydrochloric acid, and some zinc-dust added until all the fuchsin present in the liquid is reduced. The phosphine, which is not so easily reduced by zinc dust, may then be precipitated by the addition of sodium nitrate. The amount of phosphine formed varies according to the composition of the aniline oil and the temperature of the melt. It is never considerable, and very often the quantity present is so small that it is not worth while to separate it (*v.* CHRYSANILINE, vol. ii. 63).

Recovery of the arsenious acid. Formerly the residues of the manufacture of magenta were left in the factory yards or thrown into the sea. At present this is not allowed, and the manufacturers are invariably forced to recover their arsenious acid, so as to prevent the poisoning of wells and streams. The recovery, as it is now carried out, is so economical that the value of the arsenious acid obtained covers the cost of working the process. The process, which was worked out by A. Leonhardt, consists in burning the solid residues and using the heat for evaporating the arsenical liquids. The dry residue of the evaporation is introduced into the furnace, and burned along with the solid residues. Care is taken to introduce no more air than is necessary for burning the organic matter. By this precaution a complete volatilisation of the arsenic in the metallic state is obtained. The vapours of arsenic are led into a highly-heated combustion-chamber. Here they are mixed with the necessary quantity of hot air to completely burn the metallic arsenic into arsenious oxide As_4O_6. The vapours of the latter are then led through condensing chambers similar to those used in the manufacture of white arsenic. In these chambers the arsenious acid is deposited in the shape of a white powder. From time to time the chambers are opened, the arsenic is removed, and used again for the manufacture of syrupy arsenic acid by the aid of nitric acid. A certain stock of arsenic is thus sufficient to carry on the manufacture of fuchsin for an indefinite period.

2. *The nitrobenzene process.* This process was originally invented by Coupier, of Paris; but it was for the first time successfully worked on a large scale by the firm of Meister, Lucius und Brüning, of Höchst-am-Main. Other firms followed in the course of time, and at present this process has practically superseded the one with arsenic acid.

It was originally supposed that the nitrobenzene used in this process enters into the rosaniline formed, after having served as an oxidiser. At present it is generally recognised that the nitrobenzene merely acts as an oxidising agent, and that, in so doing, it is transformed into tarry matters, which are useless and remain in the residues. The nature of the nitro compound used is, therefore, of no influence on the composition of the dye-stuffs obtained. Pure nitrobenzene, or a mixture of nitrobenzene with nitrotoluene, may be used. *o*-Nitrotoluene acts more easily than any other nitro compound; it has, therefore, been used with advantage by the writer. *p*-Nitrotoluene has little tendency to act as an oxidiser. If, therefore, a mixture of nitrobenzene with the two nitrotoluenes (the so-called 'nitrobenzol for red') be used, the *p*-nitrotoluene escapes with the distillate.

The advantage of the nitrobenzene process consists, therefore, not in an economy of ingredients, but in the fact that by its application magenta free from arsenic may more easily be obtained. The yield in good crystallised fuchsin is slightly larger (if only the aniline used be taken as basis of the calculation) than in the arsenic acid process. This increase of yield pays for the increased price of the oxidising agent. In times when commercial benzene is cheap the process compares favourably with the arsenic acid process, whilst it was at a disadvantage when the prices of benzene were high. At the present time, benzene is so cheap and plentiful that the nitric acid consumed in this process is perhaps a more important item in the calculation of its cost than the benzene. For working this process it is a condition that the manufacture of aniline be carried on in the same works; the distillates are a mixture of aniline and nitrobenzene, which must be returned into the reduction process before they can be used again.

The process is worked with different proportions and in a different manner in different works. It is based on the following facts: aniline and nitrobenzene do not react upon each other; nor does a reaction take place if aniline hydrochloride be added. But if a small quantity of iron chloride be present, a reaction sets in, at a temperature of 160°. If the aniline and aniline salt used are pure, a dye-stuff of the induline group is obtained; but if *p*-toluidine and *o*-toluidine be present in the necessary proportions ordinary fuchsin is the result of the reaction. The nitro compound, however, attacks the fuchsin already formed, and part of it is therefore decomposed again. For this reason, quantitative yields cannot be obtained. At 190° the action of the nitrobenzene becomes so violent that all the colouring matter is destroyed. The greatest care is, therefore, required in this process, and the temperature should never be allowed to rise over 175°. Cold-air flues, and even arrangements for cooling with water or ice, are therefore invariably provided in connection with the melting-pots. The size of the latter has been constantly increased, because it is easier to keep large vessels at a constant temperature than small ones. Enormous pots, capable of working one or two tons of melt, have been used. Excellent arrangements for stirring should be provided. It is a good plan to make the melting-pots of spherical shape, and to give the stirrer an oblique position in this spherical pot. No water should be present in the mixture, as in this case the nitro compound is simply reduced into aniline by the ferrous chloride, and the reaction stops. The hydrochloric acid used should, therefore, be mixed with the necessary quantity of the aniline and the mixture evaporated until it solidifies into 'aniline salt cake on cooling. Sometimes the iron chloride solution is added, so that the cake obtained is intimately mixed with the iron salt. This cake is then dissolved in the rest of the aniline, the nitro compound added, and the mixture heated until the reaction sets in. Other manufacturers prefer to add iron filings or dry ferrous chloride to the mixture of aniline with aniline cake and nitrobenzene. An ingenious patent, taken out by Herran and Chaudé, proposed the use of certain double salts of the general formula $R_2Cl_6,2RCl_2$, such as ferric ferrous chloride, ferric zinc chloride, aluminium zinc chloride, and others. The addition of iron filings, originally proposed by Coupier, is not customary at present. Anhydrous zinc chloride, which has also been proposed as a means of starting the oxidising action of the nitro compound, has not proved satisfactory.

The following proportions have been proposed:

100 parts aniline for red,
50 „ nitrobenzene,
3–5 „ iron filings,

and a sufficient quantity of hydrochloric acid to neutralise two-thirds of the aniline (Häussermann). The quantity of nitrobenzene is too large; it may very well be reduced to 40 parts, or even less.

Wurtz gives the following proportions:

38 parts aniline,
17–20 „ nitrobenzene,
18–22 „ hydrochloric acid,
2 „ iron filings.

The following is Coupier's mixture:

67 parts toluidine,
95 „ nitrotoluene,
65 „ hydrochloric acid,
7 „ ferrous chloride.

The large quantity of nitrotoluene proposed in this prescription is due to the fact that only the *o*-nitrotoluene, of which about 50 parts are present in the mixture, acts as an oxidiser. The *p*-nitro compound is recovered in the distillate.

The following proportions were used by the writer in regular factory work:

400 kilos aniline for red,
222 „ hydrochloric acid, 20°Bé.,
247 „ *o*-nitrotoluene,

and the ferrous chloride prepared from

9 kilos iron borings, and
41 „ hydrochloric acid.

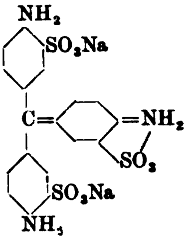
Half of the aniline is dissolved in the 222 kilos of hydrochloric acid, the solution of the ferrous chloride is added, and the whole evaporated in a stone still before being mixed with the remainder of the aniline and the nitrotoluene.

The nitrobenzene melt cannot be pushed so far as the arsenic acid melt. When finished it should not solidify into a brittle mass on cooling. It should be still soft, owing to a proportion of uncombined aniline which it still contains. This aniline must be extracted by boiling with a small quantity of dilute hydrochloric acid. After its removal, the melt becomes brittle on cooling. It is worked up in the Leonhardt extractors, in exactly the same manner as described for the arsenic acid melt.

Later improvements. It has already been said that several synthetical methods have been proposed for the manufacture of magenta, which met, however, with no success. Gradually, however, improvements have been introduced into the old melting processes, which, being based on theoretical considerations, have given favourable results. The most important of these improvements is the one described in the German patent 53937 (and additional patent) of the Farbwerke vorm. Meister, Lucius und Brüning in Höchst-am-Main, dated November 27, 1889. It consists in replacing, in the nitrobenzene process, the 'aniline for red' by a mixture of diaminodiphenylmethane and aniline. The patents refer only to the production of the diaminodiphenylmethane, which is prepared by first acting with formaldehyde (the well-known 'formalin' of commerce) upon aniline. The methylene aniline obtained is heated with aniline and aniline hydrochloride, by which means diamino-diphenylmethane is easily formed. If instead of $C_6H_5N:CH_2$, methylene aniline, any of its higher homologues be heated with the corresponding bases, the homologues of diamino-diphenylmethane are produced. By introducing these bases instead of *p*-toluidine into the magenta melt, very large yields of the dye-stuff are said to be obtained. The dye-stuff prepared by this method is sold under the name of 'Neu-Fuchsin' (new magenta).

Later on a patent was obtained by Cassella & Co., of Frankfurt-am-Main, the essence of which is probably the same. It consists in introducing methyl alcohol into the arsenic acid melt. Formaldehyde is probably thus produced, which is at once transformed into diaminodiphenylmethane. By introducing chlorinated anilines into the pararosaniline melt the chlorine substitution products of rosaniline have been obtained, which are remarkable by being much more bluish in shade than either pararosaniline or ordinary magenta (Cassella & Co., D. R. P. 21923, 1913).

Acid magenta. The ordinary fuchsin or magenta has been used for dyeing cotton, wool, and silk. But its properties make it necessary to use neutral or very slightly acid baths. This is a considerable drawback to its use on silk or wool, especially in combination with other dye-stuffs which require distinctly acid dyebaths for their successful application. It was, therefore, a decided advance to introduce a sulpho derivative of magenta into the market. This step was realised by H. Caro in 1877 (Eng. Pat. 3731, 1877; D. R. P. 2096, Badische Anilin- & Soda-Fabrik). Caro proved that magenta, which shows a marked resistance to ordinary sulphuric acid, may easily be converted into a trisulpho derivative by treatment with fuming sulphuric acid. The ordinary crystallised hydrochloride of magenta is used. It is introduced in a finely-powdered condition into fuming sulphuric acid; the mixture is then heated to a temperature not below 120° and not above 170°. Hydrogen chloride is given off, and the sulpho derivative is formed. When the operation is finished, it is diluted with water and worked up in the usual manner, by first preparing the lime-salt and then converting it into the sodium salt. The para derivative has the composition $C_{19}H_{15}N_3O_{10}S_3Na_2$, the higher homologue $C_{20}H_{17}N_3O_{10}S_3Na_2$: the ordinary acid magenta is a mixture of the two. The constitution of the para derivative may be represented by the following formula:



from which it will be seen that the sulpho-groups occupy the *ortho* positions relative to the amino groups. It forms a metallic green powder, very soluble in water with magenta colour, which disappears completely on addition of caustic alkali, the sulpho derivative of the colourless triamino-triphenyl carbinol being formed.

Acid magenta may also be obtained by acting with chlorosulphonic acid upon dry magenta base (E. Jacobsen, D. R. P. 8764, 1879; Eng. Pat. 2828, 1879).

By using the various by-products of magenta instead of the pure dye-stuff, acid derivatives of these may be obtained which prove particularly valuable for dyeing mixed shades.

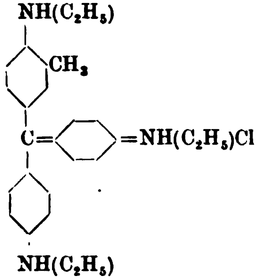
Magenta base (red base, rosein base). A large proportion of the fuchsin produced is transformed into the corresponding base, the composition of which has already been discussed. For the production of a good base, crystallised fuchsin only should be used. This is dissolved in a large volume of boiling water, and made alkaline either with milk of lime or with ammonia. In the latter case, the product obtained consists partly of the amino derivative already mentioned. No caustic alkali should be used. From the filtered solution the base settles out on cooling in crystals, which have the shape of a fern-leaf of pale-pink colour. In the air they generally become darker, because a certain amount of magenta carbonate is formed on their surface. The base thus prepared is sold for conversion into violets and blues (*q.v.*).

COLOURING MATTERS DERIVED FROM ROSANILINE.

The brilliant researches of A. W. Hofmann proved, at an early period, that rosaniline is capable of having the hydrogen atoms of its amino groups replaced by alkyl groups, and that the substances so formed are remarkable not only for the brilliancy, but also for the great variety, of their shades. Hofmann himself introduced the alkyl radicles of the fatty series into the molecule of rosaniline, and thus obtained the colouring matters which for a long time played an important part under the name of Hofmann's violets. Girard and De Laire discovered a method of introducing the phenyl and other aromatic groups into the molecule of rosaniline, and thus inaugurated the manufacture of aniline blues. It was then attempted, first by Lauth, to produce alkylated rosaniline by direct oxidation of alkylated aniline, and this method proved of great practical importance in the hands of Bardy, although the theory of the process was only understood at a much later period. Finally, a synthetical method for the production of certain alkylated rosaniline derivatives which cannot be produced by direct alkylation of rosaniline itself, was discovered by Kern, whose processes are based on the theoretical researches of Michler.

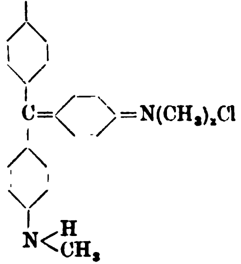
All these colouring matters will now be described, and the methods of their formation discussed.

1. **Hofmann's violet** $C_{26}H_{32}N_3Cl$, hydrochloride of triethyl rosaniline



is obtained by heating magenta base with ethyl iodide, bromide, or chloride, and a sufficient quantity of alcoholic soda solution to neutralise the acid formed in the reaction. The magenta base is prepared by decomposing a very weak fuchsin solution with milk of lime or ammonia. From the filtered solution the base crystallises in small leaflets of a pink colour. The alkylation is effected in closed vessels of copper or cast-iron, which are heated to 80°–100° by steam or in a water-bath. The trimethyl rosaniline hydrochloride, which is slightly bluer in shade, was formerly also prepared. This is no longer employed. By using less of the alkyl haloids than is necessary for completing the reaction, redder shades were obtained, which were mixtures of the mono- and di-ethyl- or methyl-rosanilines. In commerce, the more or less reddish tinge of their shade is marked by the addition of the letter R, thus: Violet R, RR, up to 5 R.

2. **Methyl violet B.** C. Lauth, wishing to find a new method for the production of Hofmann's violets, tried to oxidise methylated aniline. He obtained a violet of much bluer shade. Bardy worked out the method, which was patented by Poirrier and Chappat (Fr. Pat. 71970, dated June 16, 1866). The product obtained was proved to be the hydrochloride of pentamethyl para-rosaniline $C_{24}H_{28}N_3Cl$:—



This dye-stuff, which became of great importance, was for a long time known under the name of *Violet de Paris*. At present it is sold by the various colour works under the name Methyl Violet B to 3 B.

The mode of formation of this colouring matter is very interesting. Many researches have shown that it is best prepared from pure dimethyl aniline, which should be as free as possible from every trace of monomethyl aniline. If three molecules of dimethylaniline be oxidised into one molecule of the dye-stuff, one of the six methyl groups present serves to form the central carbon atom, whilst the other five remain combined with the amino groups of the dye-stuff formed.

The process of oxidation employed is totally different from those resorted to in the manufacture of magenta or fuchsin. Cupric chloride is used as an oxidiser at a temperature which is little above that of the atmosphere. The cuprous chloride formed is again transformed into cupric salt by the oxygen of the air. The air should, therefore, have ready access to the mixture. To fulfil this condition, a porous condition is given to the melt by the admixture of sand or other indifferent materials. Cakes are formed of the mass, and these are left on trays in a hot chamber. The following proportions have been recommended:

100	parts	sand,
10	„	dimethylaniline,
3	„	cupric nitrate,
2	„	sodium chloride,
1	„	weak acetic acid.

The cakes, which show a dull greenish colour at first, gradually assume a bronze lustre and become hard and brittle. They now contain the violet formed as an insoluble compound with cuprous chloride. To obtain the violet, the cakes should be powdered, and all soluble substances extracted with water. The double salt of violet and cuprous chloride should then be decomposed. Various means have been adopted for this purpose.

The original process consists in treating the material with a weak solution of sodium sulphide. Insoluble copper sulphide is formed, and the free violet is dissolved. From the filtered solution it may be precipitated by the addition of salt. It comes out in the shape of a gold-coloured tar of metallic appearance, which is collected and dried in jacketed pans. When dry it forms a brittle mass of metallic aspect, showing no tendency whatever to crystallise. It is sold under the name of 'Methyl violet B' or 'direct violet.'

The use of sodium sulphide has this inconvenience, that any excess of the reagent acts as a reducing agent on the violet, transforming it into its leuco compound, which cannot be separated from the violet, and impairs its strength, besides producing other complications. To remedy this drawback, several factories used gaseous hydrogen sulphide instead of the sodium compound. Hydrogen sulphide has no reducing action on the violet in neutral or slightly acid solutions. The use of this gas on a large scale is, however, extremely dangerous and accidents, which happened repeatedly, have led to the abandonment of its use.

The following methods admit of the extraction of the violet without the use of sulphides.

The first is based on the fact that, although the violet combines with cuprous chloride in the shape of its hydrochloride, this is not the case if the two be present as sulphates. If, therefore, the crude insoluble melt is boiled with dilute sulphuric acid, the violet goes into the solution together with the copper. The solution is then filtered off from the sand. If now salt were added in order to precipitate the violet, the insoluble compound would be re-formed. To prevent this, sodium sulphate (free from chloride) is used for precipitating the violet, which comes out as sulphate, whilst the copper remains in the solution. The violet sulphate is now carefully washed, re-dissolved, and re-precipitated in the shape of chloride by the addition of common salt.

Another process, which gives equally good results, is based upon the fact that the insoluble compound becomes soluble if the cuprous chloride contained in it be oxidised into cupric salt. For this purpose the crude cake is triturated with a solution of ferric chloride. It is then filtered off and washed. The violet, which has become soluble, may now be extracted with water, and precipitated by the addition of salt.

Great improvements have been effected in the melt itself. First of all, it was recognised that the cakes, if left to themselves, were apt to lose too much dimethylaniline by evaporation; they also remained insufficiently oxidised in their interior. To obviate this, the use of bread-kneading machines was resorted to, through which a current of air was blown. This current was made to pass through a vessel containing sulphuric acid, after leaving the machine. Complete oxidation was thus obtained, whilst the base which distilled over was recovered in the acid.

Later on, the quantities of the copper salt were reduced, and some potassium chlorate was added to the mixture. This yielded the necessary oxygen, the presence of a current of air became superfluous, and the evaporation of the base could be stopped by using closed vessels or kneading machines.

Another great inconvenience is the sand. It is necessary as a diluting agent, but in the after-operations it is very troublesome, being very heavy and producing great wear of the apparatus. It was, therefore, a great improvement to use clean salt instead of sand. The salt is quite as indifferent as the sand, but after having done its duty, it may be easily removed by solution, leaving the insoluble compound of the violet and cuprous chloride in the shape of a fine dark powder, which is admirably fitted for being worked up into soluble product.

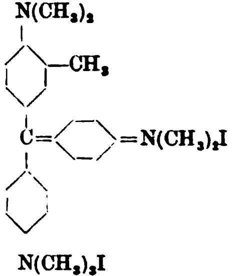
By such improvements it was possible to raise the yield of colouring matter, which at first hardly reached 45 or 50 p.c. of the dimethylaniline used, to 90 p.c. and more. If we remember that 30 p.c. of pure colouring matter is a fair yield in the manufacture of magenta, we may well understand that methyl violet, although manufactured from a much more expensive raw material than fuchsin, soon became much cheaper than its parent substance.

The yields of violet have been further increased by a curious procedure. It consists in adding some phenol to the mixture. The action of the phenol, which may be recovered, is that of a solvent; by its use the yield of violet becomes very nearly theoretical.

In the manufacture of violet, especially by the older methods, there is always some tri- and tetra-methylrosaniline formed along with the penta-methyl derivative, because the methyl groups are attacked, and transformed into formaldehyde, which escapes. The violet is, therefore, slightly redder than it ought to be. To compensate for this loss, Bardy treated his direct violet with benzyl chloride, and thus introduced benzyl groups wherever methyl was wanting. The violet of very blue shade thus obtained was brought into commerce under the name of *Methyl violet 5 B* or *Benzyl violet*. It has now lost its importance, having been to a great extent replaced by the very beautiful crystallised violets obtained by the synthetical method of Kern.

3. Iodine green and **Methyl green.** It has already been said that Hofmann's process of direct alkylation of rosaniline does not go beyond the tri-alkyl derivatives. If the action of alkyl halides be still continued, ammonium bases are formed. Thus by heating Hofmann's violet with methyl iodide in a methyl alcohol solution, Keisser obtained (1866) a green colouring matter, which was manufactured and sold for many years under the name of *iodine green*. A very similar dye-stuff was prepared from methyl-violet in a like manner by Bardy, who used, however, methyl nitrate instead of the iodide. After several explosions, the use of the nitrate was abandoned, and methyl chloride or bromide, also ethyl bromide, were used instead. The dye-stuff thus obtained was sold under the name of *methyl green*. It did not contain any iodine, and was therefore much cheaper than the iodine green, which it quickly replaced.

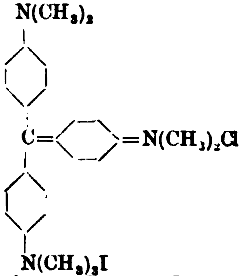
Chemically, the two may be considered as homologues of similar constitution, viz. as methyl ammonium derivatives of hexamethyl-rosaniline and hexamethyl-pararosaniline. Iodine green, being a derivative of ordinary rosaniline, contains one tolyl group:



Iodine green, $C_{27}H_{35}N_3I_2$

The methyl groups in this formula may also partly be replaced by ethyl groups if ordinary Hofmann's violet were used as a raw material.

Methyl green is the corresponding derivative of pararosaniline:



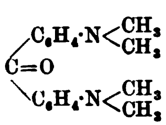
Methyl green $C_{26}H_{33}N_3Cl_2$

Both these dye-stuffs were brought into commerce in the shape of their zinc double chlorides. The iodine green formed a dark powder, whilst the methyl green formed pretty green needles or leaflets.

To prepare these dye-stuffs the violets were simply heated with the alkyl halides in closed enamelled iron vessels to 120°. Some wood spirit, or common alcohol, was added as a solvent. A pressure of 10–12 atmospheres was observed, which decreased when the reaction was finished. The crude product was dissolved in water. This solution was of dark-blue colour, because there was always some violet which remained unattacked. To separate this, the solution was shaken up with amyl alcohol, which dissolved out the violet. The green remained in the aqueous solution, from which it could be precipitated by the addition of zinc chloride and common salt. To obtain crystals, the crude green was re-crystallised from spirit.

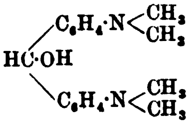
These greens have now almost entirely been replaced by the diaminotriphenylmethane derivatives already described, which are not only more brilliant in shade, but also much more stable and at the same time very much cheaper. Iodine green and methyl green are decomposed and turn a dirty violet even by the action of a gentle heat, as produced in the process of cylindering fabrics, and on many other occasions.

Pararosaniline derivatives prepared by Kern's method. Another way of preparing alkylated pararosanilines was indicated by Kern, who started from the observations published by W. Michler (Ber. 1876, 9, 716). This chemist had shown that by acting with carbonyl chloride $COCl_2$ upon dimethylaniline, dimethylaminobenzoyl chloride is formed, which acts again on dimethylaniline, yielding tetramethyldiaminobenzophenone:



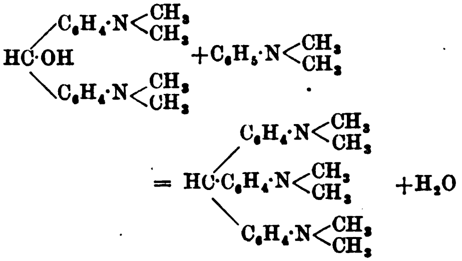
At the same time, as Michler observed, an intense blue colouring matter is formed. A. Kern (1883) followed up Michler's observations, and discovered not only the nature of the blue colouring matter, but also the conditions under which it may be obtained as the sole product of the reaction. The colouring matter proved to be pure hexamethylpararosaniline, the formation of which is due to the action of another molecule of dimethylaniline upon tetramethyldiaminobenzophenone. This action is, however, not very energetic, and must be intensified by the addition of certain substances, or by substituting for the ketone certain of its more active derivatives. A number of different processes have thus been worked out, the more important of which will now be described.

A. Kern's original modification of Michler's experiment is based upon the fact that tetramethyldiaminobenzhydrol, the secondary alcohol derived from the ketone tetramethyldiaminobenzophenone, acts readily upon aromatic bases, forming triphenylmethane derivatives. This process is described in Kern's Eng. Pat. 5450 (1883), and the corresponding D. R. P. 27032, Bad. Anilin- und Soda-Fabrik. Tetramethyldiaminobenzhydrol:



which had already been obtained by Michler by the action of sodium-amalgam upon the ketone may, according to this patent, be prepared industrially by boiling a solution of the ketone in amyl alcohol with caustic soda and zinc-dust. When the reduction is finished, the alcohol is blown off with steam, the residue dissolved in hydrochloric acid, and purified by fractional precipitation with caustic soda.

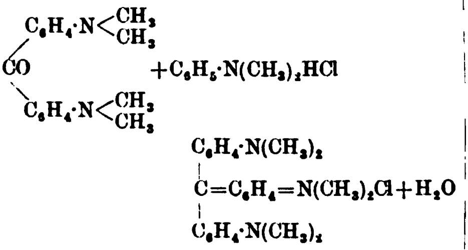
The product thus obtained may be condensed with primary, secondary, and tertiary aromatic bases, yielding in every case alkylated derivatives of paraleucaniline; thus, for instance, with dimethylaniline the leuco base of hexamethylrosaniline is formed, if the two be brought together in a solution in weak sulphuric acid



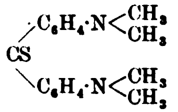
This leuco base may be oxidised into the corresponding dye-stuff by the method indicated for the production of benzaldehyde green—viz. by the action of lead peroxide upon the hydrochloride of the leuco base. The *hexamethylrosaniline hydrochloride* thus obtained is a beautifully crystallised substance, which forms green crystals if anhydrous, $C_{25}H_{30}N_3Cl$, or bronze-coloured prisms if containing water of crystallisation. In the latter case, its composition is $C_{25}H_{30}N_3Cl,8H_2O$. The power of crystallisation of this substance is very remarkable if we compare it with the ordinary violet obtained by direct oxidation of dimethylaniline; this, being a mixture of the tetra-, penta- and hexamethyl-rosanilines, shows no tendency whatever to crystallise.

If in the process described diethyl aniline be substituted for dimethyl aniline, both for the production of the hydrol base and its subsequent transformation, the result is, of course, hexaethylrosaniline, which cannot be prepared by any other process. This product is manufactured and sold under the name of '*Ethyl-purple*, 6 *B*' (ethyl violet). It is a very beautiful colouring matter, dyeing fine bluish-purple shades.

Very soon a simpler method than the one described was discovered by Kern and Caro (D. R. PP. 26016 and 29943; Eng. Pat. 4428, 1883). It was based upon the fact that the action of tetramethyldiaminobenzophenone upon dimethylaniline, which, in Michler's experiment, already had yielded a small amount of colouring matter, may be modified by the addition of certain substances, such as aluminium chloride, zinc chloride, and others. If these be present, the reaction of phosgene gas (carbonyl chloride $COCl_2$) upon dimethylaniline does not result in the formation of tetramethyldiaminobenzophenone; this is only formed as an intermediate product, which reacts at once upon another molecule of the base, forming hexamethylpararosaniline:



Many modifications of the processes here described have also been indicated and patented. Thus, instead of the carbonyl chloride, thiocarbonyl chloride $CSCl_2$ may be used, which yields with dimethylaniline the thioketone



The latter may replace the oxygen compound in all its applications.

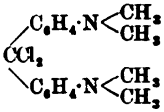
Again, trichloromethyl chloroformate

$$Cl{\cdot}CO{\cdot}O{\cdot}CCl_3$$

and similar substances have been proposed as substitutes for the carbonyl chloride.

The following is the method used at present for preparing *Crystal Violet* and *Ethyl Purple* 6 *B*: 100 kilos of dimethylaniline (or diethylaniline) are acted upon in a high-pressure pot at a temperature of 20° with 18–20 kilos of carbonyl chloride; after 24 hours' standing another 50 kilos of the base and 30 kilos powdered zinc chloride are added. The mixture is now heated to 40°–50°, and 20 kilos more of the carbonyl chloride are introduced. After 6 hours' heating to 50°, the reaction is finished. The mixture is now introduced into a still, made alkaline with caustic soda, and the excess of dimethylaniline driven off with steam. The base of the colouring matter is then dissolved in weak sulphuric acid, and precipitated in the shape of its chloride by the addition of common salt. It is then recrystallised from water.

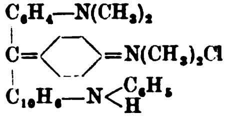
This process leads, of course, only to pararosaniline derivatives in which the three amino-groups are substituted in the same manner. Besides the hexamethyl- and hexa-ethyl derivatives, the trimethyltriphenyl derivative has been obtained from methyldiphenylamine (Amer. Pat. 327953, Kern and C. Müller). It was, therefore, a great improvement when a method was found for effecting the condensation of tetramethyldiaminobenzophenone with all kinds of primary, secondary, and tertiary bases. This method, which was worked out by Kern and H. Caro, consists in the intermediate formation of the tetramethyldiaminobenzophenone chloride:



which, being much more active than the ketone itself, reacts most easily upon bases of every description. For the manufacture of colouring matters it is not necessary to isolate the chloride, an extremely unstable substance. It is sufficient to react with phosphorus trichloride upon a mixture of the ketone with the base which is to be introduced into the triphenylmethane derivative.

This process is described in the D. R. P. 277891, the Eng. Pats. 4850 and 5038, 1884, and a large number of corresponding American patents, which contain many examples of its application to the production of dye-stuffs. Of these, however, only few have obtained lasting importance. These are basic colouring matters of a beautiful blue shade, and interesting because they are the only members of the triphenylmethane group which contain the naphthyl radicle.

Victoria blue B $C_{33}H_{32}N_3Cl$ has the constitutional formula:



It is prepared by mixing together

10 kilos tetramethyldiaminobenzophenone and

9 kilos α-naphthylphenylamine,

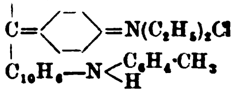
and adding

7 kilos phosphorus trichloride to the mixture.

The reaction, which sets in at once, is finished by heating to 110°. The product is dissolved in water, and the solution precipitated with salt.

A similar dye-stuff, analogous in its constitution, but of a somewhat more reddish shade, is obtained if instead of α-naphthylphenylamine, monoethyl-α-naphthylamine be used. It is known under the name *New Victoria blue R*.

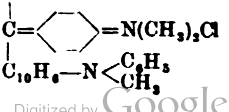
If α-naphthyl-*p*-tolylamine be taken instead of the naphthylphenylamine, and condensed with tetra-ethyldiaminobenzophenone, a blue of a very greenish shade is obtained. It is sold under the name *Night blue* (*Nachtblau*) and has the composition $C_{38}H_{42}N_3Cl$:



Another blue of very red shade is the one sold under the name *Victoria blue* 4 *R*

$$C_{34}H_{34}N_3Cl.$$

It is prepared from tetramethyldiaminobenzophenone and α-naphthylmethylphenylamine. Its constitution is probably



In describing both the green dye-stuffs derived from diaminotriphenylmethane and the old and important magenta group, it has been mentioned how much the dyer values the possibility of dyeing the useful shades which these colouring matters supply from an acid bath and of thus being enabled to combine them with all the other wool dyes capable of such application, especially the azo colouring matters. The same necessity exists for the various shades of violet here described.

This want was at first supplied by the means which had proved successful in the case of magenta, viz. by the direct sulphonation with fuming sulphuric acid of the various violets, especially the redder shades obtained by the reaction of alkyl halides upon magenta base. The colouring matters thus produced were introduced at the end of the seventies under the name of *Acid violets* to which letters denoting the shade (R and B) were added. But they did not meet with the same ready reception that had been offered to acid magenta. It is now known that the sulphuric anhydride of the fuming acid is very apt to attack the alkyl groups and thus to tarnish the shade of the violets.

The new synthetical method which had produced *Crystal violet* and its many congeners and which is apparently analogous to the synthesis of *Victoria green* and its numerous homologues, could not fail also to indicate rational methods for the production of acid violets of every conceivable shade.

Some of these methods consisted—in strict analogy to what had been done in the group of the *greens*—in introducing the benzyl group into the molecule of the dye-stuff and utilising the capacity of this radicle for sulphonation. All the variations of this method given in the description of the acid greens are admissible in the violet group. In this way the following dye-stuffs have been obtained, the structural formulae of which need not be given :—

Acid violet 4BN, *6B*, *7B* and *N*, prepared by the sulphonation of pentamethylbenzyl-pararosaniline or by the oxidation of the monosulpho derivative of pentamethylbenzyl-leucaniline.

Acid violet 6B or Guinea violet 4B. This is a disulpho derivative, obtained by oxidising the acid, which may be obtained by the condensation of dimethyl-*p*-aminobenzaldehyde with ethylbenzylaniline-sulphonic acid. The corresponding derivative of diethyl-*p*-aminobenzaldehyde is also manufactured.

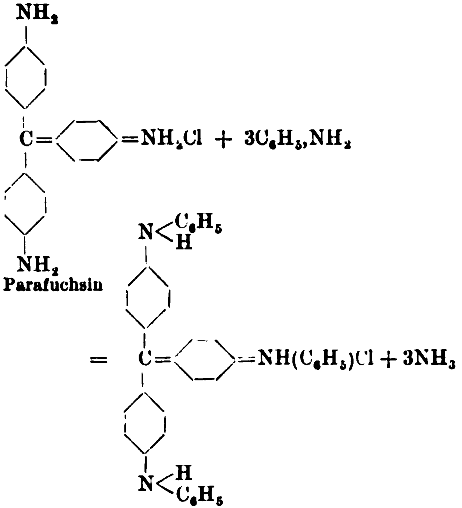
Another class of acid violets is derived from methyldiphenylamine, which may be introduced instead of dimethylaniline by all the synthetical processes described. The additional phenyl group entering into the molecule of the leuco base or the dye-stuff derived from it by oxidation is capable of carrying a sulpho group which may be introduced into it by the usual means. Thus *Alkali violet 6B* and *Acid violet 7B* can be prepared, whilst in *Acid violet 7BN* ready formed methyldiphenylsulphonic acid is condensed with dimethyl-*p*-aminobenzoic acid.

The process of introducing elements capable of being sulphonated into the synthesis of rosaniline derivatives may be carried still farther. Thus a useful dye-stuff, called *Wool green*, is manufactured by several firms by condensing tetramethyldiaminobenzophenone (Michler's ketone) with β-naphthol and subsequently sulphonating the insoluble dye-stuff so obtained.

Rosaniline blues or **phenylated rosanilines.** These are of great importance, forming by far the majority of blue aniline dyes in the market. The chemistry of these compounds is, however, extremely complicated. The blues sent into commerce are not chemically pure substances, but mixtures of various isomerides; it is very difficult to classify them. Moreover, they are known under a great variety of fancy names, many of which are applied to products of different composition by different firms. The following is an attempt to classify the various blues.

It has already been shown that a considerable difference exists between pararosaniline hydrochloride or parafuchsin and the ordinary fuchsin of commerce. The former is a uniform compound $C_{19}H_{18}N_3Cl,4H_2O$, whilst the latter is a mixture of parafuchsin with at least two isomeric homologues. Both these substances may be phenylated; their phenyl derivatives are blue colouring matters of great intensity and beauty. But a greater difference is found to exist between the phenyl derivatives of pararosaniline and those of ordinary magenta than even between the two kinds of fuchsin themselves.

The method of phenylation is very remarkable, and quite different from the methods of substituting fatty radicles for hydrogen in the amino groups of rosaniline. The general method in this case consisted in treating rosaniline base with the halogen derivatives of these radicles. Owing to the great stability of chlorobenzene C_6H_5Cl, the same process cannot be applied to the phenylation of rosaniline. This takes place, however, with great facility if we allow aniline to act upon rosaniline, ammonia being given off as a by-product :



Triphenyl-pararosaniline hydrochloride
(Rosaniline blue)

This method of phenylation, which has been indicated by Ch. Girard and G. de Laire, is invariably resorted to. It cannot, however, be applied on a practical scale to the hydrochloride, as assumed for simplicity's sake in our equation. Experience has shown that organic acids must be used in order to get good results. The majority of organic acids have been tried for the purpose; at present, however, only two are used, which give distinctly different results, viz. acetic and benzoic acids. The reason for this difference has not been definitely ascertained, but it is a fact known to every manufacturer that blues of a greenish shade can only be obtained with benzoic acid, whereas acetic acid yields more reddish compounds.

The phenylation of rosaniline cannot be pushed further than the formation of triphenylrosaniline. The tetra-, penta-, and hexaphenyl derivatives are not known. But even the formation of triphenylrosaniline, such as it is indicated by our equation, takes place in three successive stages, the phenyl groups entering the molecule one after another. It is, however, practically impossible to separate these stages. If, in the beginning of a blue melt, a certain amount of mono-phenylrosaniline be formed, the reaction proceeds simultaneously on this and on rosaniline, which has not yet been attacked; thus, in a second phase, monophenyl and diphenyl rosaniline, and rosaniline (which has not yet been attacked) will be present together. To these the triphenyl compound will presently be added, a very complex mixture being the result. By a more prolonged action it is possible to eliminate rosaniline itself and its monophenyl derivatives completely from the mixture. But some diphenylrosaniline will always remain present. Moreover, all these compounds seem to exist in various isomeric modifications. It is a mixture of these which forms the ordinary *crude* or *Opal blue.*

If, instead of pararosaniline, the ordinary rosaniline of commerce be used for the production of the blue (as is the case in most instances) the product becomes even more complicated by the presence of the homologous compounds. Some process of separation which splits up the crude product into fractions of different shades and reactions must be resorted to; and although some of these are crystallised, it cannot be said with certainty that they represent chemically pure individuals.

Mono- and di- phenylpararosaniline have hitherto not been prepared in a pure state. Nothing can, therefore, be said of their properties.

Triphenylpararosaniline hydrochloride

$C_{37}H_{30}N_3Cl$

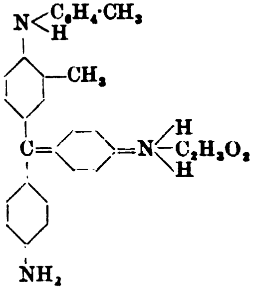
is the purest and brightest blue known. It is now invariably prepared by the phenylation of pararosaniline, but it may also be obtained by melting together diphenylamine and oxalic acid. The formic acid evolved in the decomposition of oxalic acid serves to link together three molecules of diphenylamine into one of triphenyl leuco aniline, which is then slowly oxidised into the rosaniline compound. It was this method which was formerly used for the production of this blue, which therefore is still frequently described as *Diphenylamine blue*; it is also sometimes called *Methyl blue*, because methyldiphenylamine was occasionally used for its production. Other names for the same product are:

Bleu direct, bleu lumière, bleu de Lyon, bleu de Mulhouse, bleu de nuit, bleu de Paris, light blue, night blue, Paris blue, Bavarian blue.

This product forms a microcrystalline powder of a bronzy appearance, completely insoluble in water, sparingly soluble, with a brilliant blue colour, in spirit. Its transformation into the soluble diphenylamine blues of commerce will be described hereafter.

When the same process of phenylation (the particulars of which will be given below) is applied to the ordinary rosaniline of commerce—which is, as will be remembered, a mixture—various products are obtained. Of these the following may be said to have been isolated:—

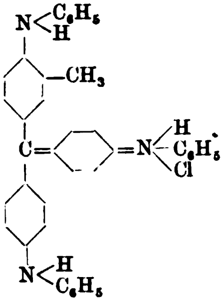
Monophenyl rosanilines. These are the product of a very moderate phenylation. They are still soluble, in the shape of their acetates, in water, and dye fine purple shades. They have now, owing to the greater cheapness of methyl violets, almost completely disappeared from the market, in which they formerly played an important part under the name of *Regina purples* or *Regina violets.* It was customary to prepare them, not by the action of pure aniline on magenta acetate, but rather by that of the recovered oils or *échappés* from the magenta process, which contained a large proportion of o-toluidine. The action of the latter is slower than that of aniline; it is, therefore, easier to stop the reaction before a considerable proportion of the diphenyl or ditolyl rosaniline is formed. The regina purples consisted, therefore, to a great extent of the *o*-tolylrosaniline, the acetate of which is represented by the following formula:



Regina purple

Diphenylrosanilines. These were invariably obtained, together with the regina purples, from which they are distinguished by their complete insolubility in water. They are, however, still of a purple shade; they are invariably present to some extent in crude tri-phenylrosaniline blue, if the latter be prepared with acetic instead of benzoic acid. This is the reason why such blue is always of a redder shade than the blue prepared with benzoic acid, in which the proportion of diphenyl derivatives is reduced to a minimum. A product which consists chiefly of diphenyl rosanilines, is known under the name of *spirit purple, spirit violet*, or *opal violet*; it has also been sold as *regina spirit purple.* From it the *soluble violets* and *purples* and *alkaline purples* of commerce are derived by sulphonation.

Triphenylrosanilines. The triphenyl derivatives of ordinary rosaniline may be subdivided into two classes: crystalline and uncrystallisable blues. The former may be extracted from every crude blue melt prepared with benzoic acid. They represent in a state of approximate purity the triphenyl derivative of the higher homologue of pararosaniline, and may therefore be represented by the following formula:



It is to this product, which forms the base of the high-class alkaline and water blues of commerce, that one should reserve the name of *Opal blue*, which has, however, been indiscriminately applied to a number of various products. This opal blue forms, in the shape of its pure hydrochloride, a mass of distinct, though very small, glistening crystals of a greenish brass-colour. It is completely insoluble in water and in spirit. If it be treated with alcoholic caustic soda, the free base is obtained in the shape of a tarry substance from which the acetate may be prepared by dissolving it in glacial acetic acid, and re-precipitating with water. This acetate is soluble in spirit, and, though sparingly, also in water. It was formerly sold and used under the name of *Opal blue* 6 *B for cotton*, *Gentian blue*, *Hessian blue*; also the names of *Bleu lumière*, *Bleu de nuit* (originally used for the para derivative), were occasionally applied to it. In Germany it was sold under the name of *Feinblau*, *Sprit-blau*. The latter expression is applied, however, to all blues soluble in spirit, not only to this acetate. Its use has been much restricted of late, owing to the unwillingness of the dyer to use spirit in the dye-bath.

The second class of triphenyl derivatives of ordinary rosaniline, comprises the uncrystallisable portions of crude blue melts. They contain a mixture of triphenyl- and diphenylrosanilines in various proportions, quite inseparable by the means which are at our disposal. They are (in the shape of hydrochlorides) insoluble in water, soluble in spirit. Caustic soda transforms them into a mixture of the corresponding bases, which are tarry masses. Their shade varies from a purplish-blue to a distinct clear blue of great strength and purity which, however, always shows a purplish hue if looked at by artificial light. This blue forms the starting-point for the production of innumerable brands and qualities of alkaline and water blues, varying in their shade and in the purity and strength of their colour. They are designated, according to the redness of shade, by the letters 3 R, 2 R, R, B, 2 B, and 3 B, whilst 4 B, 5 B, and 6 B may be said to be reserved for the derivatives of the true opal blue of varying purity. A large number of fancy names, such as *China blue*, *Marine blue*, *Serge blue*, &c., have been invented for this kind of blues.

Besides these blues a special kind of low-class blue should be mentioned which, under the name of *Blackley blue*, has enjoyed, and still enjoys, much favour, especially for dyeing paper-pulp, and also for the production of cheap woollen materials. This is the sulphonation product of a peculiar kind of phenyl rosaniline, prepared by acting with aniline upon crude magenta. It is consequently very impure, but also very cheap. It contains a mixture of the phenylation products of all the substances contained in crude magenta.

Tri-*p*-tolylrosaniline has been prepared by acting with *p*-toluidine in the presence of benzoic acid upon ordinary rosaniline base. It is a blue of remarkable beauty and brilliancy of shade, which offers, however, great resistance to the process of sulphonation. It has, therefore, only been manufactured and sold in the shape of its hydrochloride, which is soluble in spirit. It is sold for dyeing cotton under the name of *Grünlichblau* (Höchst) or 6 *B extra opal blue* (English manufacturers). It has largely gone out of use of late years.

Manufacture of blues. An immense number of prescriptions for blue melts has been published, and a larger number still circulates amongst manufacturers. It would be perfectly useless to reproduce any of them. The principles upon which they are based may be thus briefly stated:—

For the production of good blues a perfectly pure magenta base is the first requirement. For its preparation crystallised fuchsin only should be employed. If crude magenta or any of the magenta residues (*cerise*, *grenadine*, &c.) be used, the base obtained can only be employed for the production of *Blackley blues*. Pure pararosaniline, the base prepared from parafuchsin (*Neu-fuchsin*), should be used for the production of the so-called diphenylamine or methyl-blues (direct blues); whilst crystallised base from ordinary fuchsin forms the starting-point for all the ordinary blues from 4 R to 6 B, as well as for regina purples.

The second condition for the production of good blues is the use of very pure aniline, perfectly free from toluidine. It is in the manufacture of blues that the necessity of operating with pure aniline was first felt. The term *aniline for blue* was, therefore, and is still occasionally, applied to perfectly pure aniline, boiling within one degree, and having a specific gravity of 1·0268–1·0270. Such aniline can only be prepared from pure crystallisable benzene.

If these two conditions—pure magenta base and pure aniline—be fulfilled, the shade of the blue obtained is still dependent upon:

1. The proportions of base and of aniline in the melt. It may be said that greenish blues will only be obtained if a very large excess of aniline be used, whilst reddish blues are produced in melts rich in magenta base.

2. The time and temperature of the melt. The formation of blue begins below 100°. It proceeds quickly at a higher temperature; 120°–140° may be assumed to be the most favourable temperature. From 140°–180° certain impurities (diphenylamine ?) are formed, which impair the tendency of crystallisation of the blue. The temperature of high-class blue melts should therefore not be raised above 140°. The

time required by a blue melt depends upon the proportion of base to aniline, and, to some extent, the quantities operated upon. The process proceeds quickly in highly-concentrated melts. Melts for high-class blues, which contain a large proportion of aniline, require prolonged heating —20 hours, and even more, before being finished. As a rule, the progress of the melt is tested by placing a drop of the melt on filter paper moistened with spirit. The gradual change of colour may thus be observed with great accuracy. When the melt is finished, there should be no reddish rim visible in the spot produced on the paper.

3. The nature and proportion of the acid used in the melt. It has already been said that organic acids only should be used, the action of hydrochloric acid being too slow. Acetic and benzoic acids are now used exclusively. The action of acetic acid is quicker than that of benzoic acid, but it seems impossible to transform all the rosaniline into its triphenyl derivative by the use of acetic acid. Benzoic acid acts more slowly, but it continues its action until all the rosaniline is transformed into the triphenyl derivative. At the same time, the whole of the melt is, even with benzoic acid, not entirely transformed into crystallisable opal. Moreover, acetic acid produces (by its simultaneous reaction on aniline) some acetanilide, which remains in the blue and is apt to prevent its subsequent crystallisation, whilst no benzanilide is formed by heating aniline with benzoic acid. For these reasons acetic acid is employed in the production of low-class reddish-blues (in concentrated melts), whilst benzoic acid is used only for the production of high-class opals. The greater part of the benzoic acid may be recovered from the melt, whilst the recovery of the acetic acid does not pay.

There is no advantage in using other acids instead of acetic and benzoic acid. As a rule, it may be said that the fatty acids (formic, butyric, valeric acids) act similarly to acetic acid, whilst the aromatic acids (toluic, phthalic, cinnamic acids) may take the place of the benzoic acid.

Upon these conditions all the prescriptions for blue melts are based. Taking the quantity of magenta base to be operated upon as unity, the quantity of aniline added varies from four to twenty-five times its weight, the quantity of the organic acid from $\frac{1}{10}$ to $\frac{1}{2}$. The conditions of time and temperature have already been stated.

The apparatus necessary for blue-making is very simple so far as the melt is concerned, enamelled cast-iron pots with a lid and stirrer being always used. In the early times of the manufacture of aniline colours it was believed that blue melts could only be made in glass, and on a very small scale. In the 'Fuchsin' factory at Lyons the blue was therefore manufactured in large numbers of glass flasks heated in a sand-bath. At present it is believed that blue melts are best under control in large quantities; large melting-pots are therefore used as a rule. While the melt is in progress ammonia is given off, which carries a certain amount of aniline away. It is advisable to condense this aniline, and to absorb the ammonia by water or sulphuric acid.

When the melt is finished it must be worked up. This may be done by a variety of methods. Of these the simplest—which is, as a rule, resorted to in the manufacture of low-class and Blackley blues—consists in neutralising the melt with a quantity of caustic soda just sufficient to saturate the acid added to the melt. The excess of the aniline is then driven off with steam and recovered. The blue base remains in the still, and is run out whilst still hot, in a tarry state, together with the water. On cooling, it solidifies into a very brittle mass, which may be powdered, dried, and subjected to the process of sulphonation to be described hereafter.

For the production of high-class blues this simple process cannot be adopted. A separation of the crystallisable opal from the uncrystallisable blue, which invariably accompanies it, must take place, and for this separation the melt requires a special treatment. For this there are two distinct processes, of which one is very complete, although costly, because it requires large quantities of spirit. We may call it the *English process*, because it was worked and carried out chiefly in English factories. The other process, which is now used in most of the German works, is very rapid, and requires but little spirit. On the other hand, it does not give so pure a product; we may call it the *German process*.

The English process is the final outcome of the original French process for working up the blue melts, which consisted in boiling them out with dilute hydrochloric acid. The aniline was dissolved out together with the organic acid present, whilst the blue remained in the shape of its hydrochloride as a fine blue precipitate, which was filtered off and washed. It was then ready for sulphonation. When it was discovered that this blue was a mixture of different colouring matters it became customary to separate these by boiling the crude blue with spirit. This dissolved out the lower-class blues, leaving a better product as a residue. By repeating this process frequently, a residue was obtained at last which was quite insoluble in spirit. This represented the purest opal blue obtainable. It was by this tedious process that the once famous 'Bleu Mavi,' or 'Bleu MAVI' was obtained in France and Switzerland. The improved English process much simplified things, and at the same time gave better yields and a purer colour by producing the opal blue in a crystallised condition, in which it is totally insoluble in spirit. This process consisted in adding to the melt (prepared with benzoic acid and a large excess of aniline), while still hot, a certain quantity of aniline hydrochloride; on cooling, the opal blue, being gradually converted into the hydrochloride, settled out in small glistening crystals, whilst the low-class blue remained dissolved in the aniline. The opal was then filtered off, and washed with spirit until quite pure. If necessary, it could be re-converted into base by treatment with alcoholic caustic soda. The base, re-dissolved in aniline, could again be converted into hydrochloride by again adding aniline hydrochloride. The opal then came out in very fine crystals, which represented the blue in a state of greatest purity. The aniline liquors obtained from these crystallisations had to be distilled in order to recover the spirit. They were then made alkaline in order to decompose the aniline hydrochloride present, the aniline was driven off by steam, and the remaining low-class blue obtained in the shape of base as described. Owing to the large quantities of spirit used for washing the crystallised opal, and the consequent loss of spirit by evaporation, this process (which may be recommended for laboratory experiments) was costly, and unable to compete with the rapid and cheap German process.

The German process is based upon the fact that the crystallisable blue opal is insoluble in a very hot solution of aniline hydrochloride, whilst the common non-crystallisable blues are soluble in this liquid. The solution of the aniline salt must, however, be so concentrated (in order to act properly) that it would solidify into a mass of crystals if cooled in the least degree. It is rather fused aniline hydrochloride that is required, and not an actual solution of the salt in water. In order to operate properly with such liquids, closed vessels must be used. The following is the principle upon which the plant in the majority of German works is constructed.

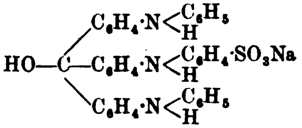
Near the melting-pot a battery of closed iron vessels, lined with lead, is erected. The first of these is filled with a quantity of hydrochloric acid, just sufficient to neutralise the aniline contained in the blue melt. The melt, when finished, is introduced into this vessel by means of air pressure. The vessel is fitted with a stirrer, which stirs up the mixture into a homogeneous mass. This is then pressed into a second vessel, which contains some filtering arrangement, upon which the blue crystals are deposited. The liquid which issues from this vessel is diluted with water, when the common blue hitherto dissolved in it is quickly deposited. The blue crystals remaining on the filter are washed with water, and may be purified by boiling them with spirit.

Blues soluble in water. Very little of the blue that is manufactured is used in the opal state, viz. soluble in spirit. By far the largest proportion of it must be transformed into products soluble in water in order to become a marketable article. For this purpose sulphonation is resorted to.

The sulphonation of triphenylrosaniline takes place very easily, the phenyl radicles attached to the amino groups being readily substituted by the sulpho group SO_3H. As there are three of these phenyl radicles present, three sulpho groups may be introduced into the molecule of the blue. The pure, crystallisable, high-class opal blue is more easily sulphonated than the common blues. The sulphonation takes place in progressive stages, one sulpho group being introduced after the other. It is difficult to introduce more than two sulpho groups by the use of ordinary sulphuric acid. Fuming sulphuric acid must be resorted to in order to produce the trisulpho derivative. As this, however, is hardly ever required, being much too soluble for the purposes of the dyer, common sulphuric acid is invariably used, but the 'extra-strong' quality of 95–97 p.c. H_2SO_4 is, as a rule, preferred.

If this acid be allowed to act upon an aniline blue, the reaction begins at about 30° and results at first in the formation of the monosulpho derivative. The following are its properties:

In the free state triphenylrosaniline monosulphonic acid forms blue flakes, which are quite insoluble in water, in a solution of sodium bicarbonate, or even in weak ammonia. Sodium carbonate dissolves it on boiling; caustic soda in the cold. The solutions are perfectly colourless. They contain, in fact, the sodium salt of monosulphotriphenyltriaminotriphenylcarbinol:



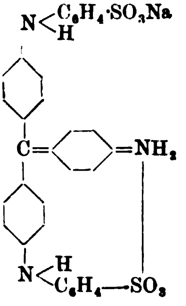
The dry sodium salt is jet black.

This compound has the curious property of combining with wool in an alkaline bath. The wool remains colourless, but after being washed with water it becomes brilliantly blue if immersed in weak sulphuric acid.

This curious property, discovered by Nicholson, has been made use of by wool dyers, who prefer the 'alkaline' or 'Nicholson' blues to all others for the production of bright and brilliant blues.

The alkaline blues originally manufactured by Nicholson and other makers were as nearly as possible the pure sodium salts of the monosulpho derivative. Owing to the difficulty of dissolving them even in boiling water, another kind of alkaline blues was produced later on; these new alkaline blues contain a proportion of the disulpho derivative. They form blue powders, easily soluble in water, giving a solution which is distinctly blue. The use of these new alkaline blues is exactly similar to that of the old quality.

If the sulphonation of the opal blue be carried farther by raising the temperature and allowing the reaction to continue for a longer period, the monosulpho acid gradually disappears and is replaced by the disulpho derivative. This is insoluble in weak sulphuric acid, but rather soluble in pure water, with an intensely blue colour. Its sodium salt forms bright coppery masses soluble in water with a blue colour. This salt contains probably the compound represented by the following formula:



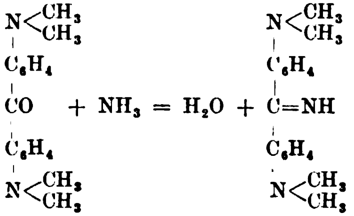
The disulpho derivatives of the various classes of triphenyl-rosanilines are known under the names of *Cotton blue, Water blue, China blue, Navy blue, Guernsey blue,* and many others, which are again sub-divided by the use of the letters R and B. Thus a 6B cotton blue is the disulpho acid of a very high-class, crystallisable Opal blue, whilst a 4R Guernsey or Navy blue would be a reddish-tinted blue, manufactured from an opal prepared with acetic acid and a small excess of aniline in the melt.

The process of sulphonation, though very simple in theory, requires great care and attention on the part of the manufacturer. The sulphonation is carried on in cast-iron pots into which the necessary quantity of sulphuric acid is introduced. The opal blue, which should be finely powdered and perfectly dry, is then stirred in, and the temperature raised gradually. Samples should be drawn from time to time, and the precipitate produced by the addition of water must be examined as to its solubility in water, weak ammonia, sodium carbonate, and caustic soda. When the desired degree of solubility is obtained, the liquid is poured into water, and the blues filtered off and carefully washed. When quite free from acid, they are dissolved in the necessary quantity of caustic soda; the solution is then filtered, and evaporated to dryness in jacketed pans. Cotton blues should be freed from the excess of sulphuric acid by the addition of slaked lime. The solution of the calcium salt is filtered and converted into the sodium salt by double decomposition with sodium carbonate. After another filtration, the solution of the blue is evaporated to dryness. Certain artifices are required to produce porous masses, such as the brand known as *China blue*, which is manufactured for export, and is required to possess a given bulk for a given weight.

Appendix to basic triphenylmethane colouring matters.

Auramine. This dye-stuff, although a derivative of diphenylmethane, is so closely connected with the manufacture of crystallisable violet that it cannot be omitted from this article.

It has been shown that crystal violet, as well as Victoria blue and other dye-stuffs, are manufactured from dimethyl and diethyl diaminobenzophenone. Now, if these ketones be heated with ammonium chloride in the presence of zinc chloride, an interesting reaction takes place at the temperature of 150°–160°. The oxygen of the ketone is replaced by the imino group NH, thus:



$$\begin{array}{c} N{<}^{CH_3}_{CH_3} \\ | \\ C_6H_4 \\ | \\ CO \\ | \\ C_6H_4 \\ | \\ N{<}^{CH_3}_{CH_3} \end{array} + NH_3 = H_2O + \begin{array}{c} N{<}^{CH_3}_{CH_3} \\ | \\ C_6H_4 \\ | \\ C{=}NH \\ | \\ C_6H_4 \\ | \\ N{<}^{CH_3}_{CH_3} \end{array}$$

The imides thus obtained are yellow colouring matters, and have received the name of *auramines*. The auramine of commerce is iminotetramethyl-di-*p*-amino-diphenylmethane hydrochloride, containing one molecule of water of crystallisation:

$$C_{17}H_{21}N_3{\cdot}HCl,H_2O.$$

It forms a yellow powder easily soluble in water. It is exclusively used for dyeing and printing on cotton.

Substituted auramines may be obtained by using the hydrochlorides of primary bases instead of sal-ammoniac. Thus a phenylat auramine of orange colour may be produced by acting with aniline hydrochloride upon tetramethyldiaminobenzophenone.

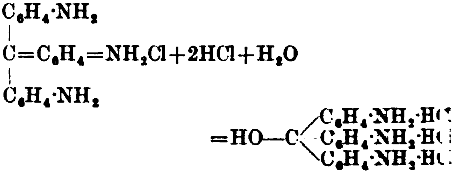
The auramines were discovered by Caro and Kern in 1884. They form the subject of the Eng. Pats. 5512, 1884, and 5741, 1884, and the D.R.PP. 29060 and 31936. (*See* art. AURAMINE, vol. i. 338.)

II. THE AURIN GROUP.

The members of this group contain oxygen in the place of the pentavalent nitrogen of the preceding one. If magenta and its congeners may be considered as quinone-imides, the aurins are the corresponding quinones.

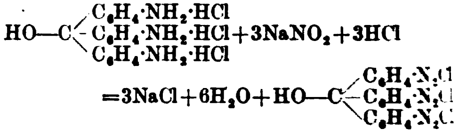
The generic relation between the fuchsin and the aurin groups will be best seen by showing how the typical representative of the former, parafuchsin, may be transformed into the first representative of the aurin group, aurin itself.

We know that parafuchsin, if treated with an excess of acid, is transformed into the triacid salt of triaminotriphenylcarbinol:



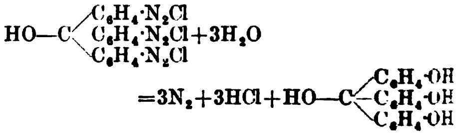
$$\begin{array}{l} C_6H_4{\cdot}NH_2 \\ | \\ C{=}C_6H_4{=}NH_2Cl+2HCl+H_2O \\ | \\ C_6H_4{\cdot}NH_2 \end{array} = HO{-}C{\begin{array}{l} \diagup C_6H_4{\cdot}NH_2{\cdot}HCl \\ {-}C_6H_4{\cdot}NH_2{\cdot}HCl \\ \diagdown C_6H_4{\cdot}NH_2{\cdot}HCl \end{array}}$$

Now this salt, if treated with nitrous acid, is transformed into the corresponding diazonium compound.



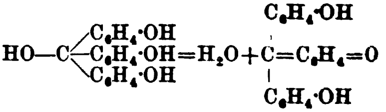
$$HO{-}C{\begin{array}{l} \diagup C_6H_4{\cdot}NH_2{\cdot}HCl \\ {-}C_6H_4{\cdot}NH_2{\cdot}HCl \\ \diagdown C_6H_4{\cdot}NH_2{\cdot}HCl \end{array}}+3NaNO_2+3HCl = 3NaCl+6H_2O+HO{-}C{\begin{array}{l} \diagup C_6H_4{\cdot}N_2Cl \\ {-}C_6H_4{\cdot}N_2Cl \\ \diagdown C_6H_4{\cdot}N_2Cl \end{array}}$$

This, on being boiled with water, loses nitrogen and is transformed into trihydroxytriphenylcarbinol



$$HO{-}C{\begin{array}{l} \diagup C_6H_4{\cdot}N_2Cl \\ {-}C_6H_4{\cdot}N_2Cl \\ \diagdown C_6H_4{\cdot}N_2Cl \end{array}}+3H_2O = 3N_2+3HCl+HO{-}C{\begin{array}{l} \diagup C_6H_4{\cdot}OH \\ {-}C_6H_4{\cdot}OH \\ \diagdown C_6H_4{\cdot}OH \end{array}}$$

The latter loses, in *statu nascendi*, one molecule of water, being transformed into its inner anhydride, aurin:



$$HO{-}C{\begin{array}{l} \diagup C_6H_4{\cdot}OH \\ {-}C_6H_4{\cdot}OH \\ \diagdown C_6H_4{\cdot}OH \end{array}} = H_2O+\begin{array}{l} C_6H_4{\cdot}OH \\ | \\ C{=}C_6H_4{=}O \\ | \\ C_6H_4{\cdot}OH \end{array}$$

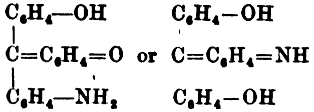
Thus aurin is parafuchsin in which all nitrogen has been replaced by oxygen.

This mode of formation has long been known, not for aurin itself, but for its higher homologue, rosolic acid, which was prepared from the ordinary fuchsin or magenta by the process described. The many co-ordinate points of aurin and rosolic acid were recognised at an early period. On the other hand, chemists were aware of the distinct difference between aurin and rosolic acid, which is just as considerable as that existing between parafuchsin and its higher homologue.

When an insight into the nature of the fuchsin group had been obtained, the knowledge of the constitution of the aurin group followed as a natural consequence.

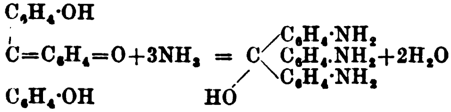
But even before this was the case, another connection was discovered between aurin and fuchsin.

It had long been known that aurin (the mode of formation of which will be given later on) may be modified by heating it with alcoholic ammonia. F. Persoz produced a red dye-stuff, which he called *Pæonine*, by this process. This had, in all probability, the following constitution:



$$\begin{array}{l} C_6H_4{-}OH \\ | \\ C{=}C_6H_4{=}O \\ | \\ C_6H_4{-}NH_2 \end{array} \quad \text{or} \quad \begin{array}{l} C_6H_4{-}OH \\ | \\ C{=}C_6H_4{=}NH \\ | \\ C_6H_4{-}OH \end{array}$$

In 1878, Dale and Schorlemmer, whose researches on aurin are of great importance, showed that aurin, by very prolonged heating with alcoholic ammonia, may be transformed into pararosaniline

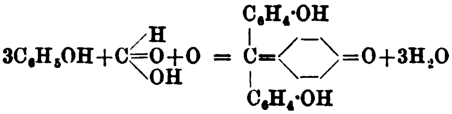


$$\begin{array}{l} C_6H_4{\cdot}OH \\ | \\ C{=}C_6H_4{=}O \\ | \\ C_6H_4{\cdot}OH \end{array} + 3NH_3 = \begin{array}{l} \quad C_6H_4{\cdot}NH_2 \\ C{-}C_6H_4.NH_2 \\ \quad C_6H_4{\cdot}NH_2 \\ HO \end{array} + 2H_2O$$

Thus the connection of the two typical dye-stuffs was definitely established. At present we know that the aurin group contains the acid counterparts of the basic members of the fuchsin group. A considerable number of them are known and described in chemical literature. As, however, almost all of them are of no practical value it would be useless to enumerate them in this article. We will therefore describe only those substances of the aurin group which are of some practical interest. There are very few of them.

1. **Aurin** $C_{19}H_{14}O_3$. The discovery of this substance, or one very nearly related to it, dates as far back as 1834, when F. Runge, the pioneer of the chemistry of coal-tar, observed that crude carbolic acid (containing cresol) was transformed into an acid red dye-stuff by oxidation. Later on (1859), Kolbe and Schmitt and F. Persoz simultaneously observed that pure phenol, when heated with oxalic acid, or with oxalic acid and sulphuric acid, was transformed into a similar red substance. The manufacture of the new dye-stuff was first taken up in Lyons by the firm of Guinon and Marnas. Later on, it was carried out on a large scale by C. Calvert and by C. Lowe; also by Roberts, Dale, & Co., in Manchester. The crude aurin thus obtained is a non-crystallisable, brittle, pitchy mass, of a brilliant green metallic aspect, insoluble in water, but soluble in caustic soda solution, with a magnificent red coloration. It dyes silk and wool from an acid bath, producing an orange shade on these fibres. It was much used on silk in former days, but its use has been abandoned since the introduction of the azo-colouring matters, which produce brighter and faster shades.

The researches of Dale and Schorlemmer, Zulkowski, and others have shown that common aurin consists of a mixture of a number of substances which, in a pure state, are well crystallised. Of these, aurin itself $C_{19}H_{14}O_3$, oxyaurin $C_{19}H_{16}O_6$, methylaurin $C_{20}H_{16}O_3$, and pseudorosolic acid $C_{20}H_{16}O_4$, may here be mentioned. All these substances are produced by the action of nascent formic acid (generated from the oxalic acid) upon phenol. This mode of formation of aurin itself may be represented by the following equation:

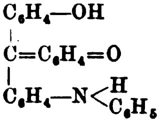


A large number of other reactions have been observed in which aurin is formed to a greater or lesser extent. Thus, for instance, it is obtained by acting with formaldehyde, with iodoform, with chloroform and caustic potash on phenol. These reactions have never attracted the attention of manufacturers, aurin having lost its practical interest.

The sodium salt of crude aurin is known in commerce under the name of *Yellow Corallin*.

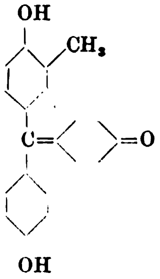
2. **Pæonin**, *corallin red, aurin red* is the sodium salt of the reaction product of alcoholic ammonia upon aurin, which has already been mentioned and the constitution of which is given above.

3. **Azulin** is a similar product, of a dirty violet shade, obtained by heating aurin with aniline. It is probably phenylated pæonin:



$$\begin{array}{l} C_6H_4{-}OH \\ | \\ C{=}C_6H_4{=}O \\ | \\ C_6H_4{-}N{<}^{H}_{C_6H_5} \end{array}$$

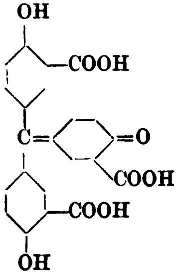
4. **Rosolic acid** is the name which was originally given by Runge to the oxidation product of crude carbolic acid. For a long time it was considered to be identical with aurin. At present this name is reserved for the product obtained from the ordinary fuchsin of commerce by the diazotising process. It forms magnificent blue needles, which, being homologous to true aurin, have the composition $C_{20}H_{16}O_3$:



It dyes silk and wool orange shades, similar to those obtained with aurin. It is of no practical interest (*v.* AURIN AND ROSOLIC ACID, vol. i. 340).

5. **Chrome violet** $C_{22}H_{13}O_9Na_3$ is the only member of the aurin group which is of

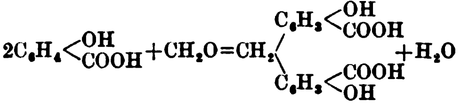
considerable practical value. It is the sodium salt of aurin-tricarboxyl acid:



It was discovered in 1889 by Sandmeyer, and patented (D. R. P. 49970, J. R. Geigy). It is prepared by acting with formaldehyde, or with a mixture of methyl alcohol and sodium nitrite, upon a solution of salicylic acid in sulphuric acid. The carboxyl groups are in the *ortho*-position to the hydroxyl groups. The result of this arrangement is that the dye-stuff combines readily with metallic mordants of the iron group, and especially with chrome mordant, producing violet shades of considerable fastness on cotton. It is chiefly used for printing on cotton.

The process patented for the production of chrome violet is interesting, because it forms a general and excellent synthetical method for the production of the aurins. It is strictly analogous to the synthetical method adopted for the production of 'Neu-fuchsin' by the 'Farbwerke' of Höchst. Two stages may be distinguished in the process:

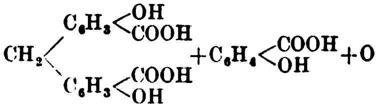
(*a*) In the first stage, formaldehyde (or methylal) acts upon two molecules of the phenol—in the case of chrome violet, salicylic acid—forming the diphenylmethane derivative (methenyl salicylic acid):



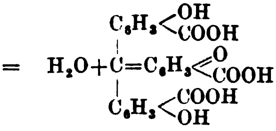
$$2C_6H_4{<}^{OH}_{COOH} + CH_2O = CH_2{<}\begin{array}{l} C_6H_3{<}^{OH}_{COOH} \\ C_6H_3{<}^{COOH}_{OH} \end{array} + H_2O$$

This reaction may be facilitated by the addition of condensing agents, such as hydrochloric acid and others.

(*b*) In the second stage, the diphenylmethane derivative is simultaneously condensed and oxidised with another molecule of the phenol into the corresponding aurin by the mixture of sulphuric acid and sodium nitrite:



$$CH_2{<}\begin{array}{l} C_6H_3{<}^{OH}_{COOH} \\ C_6H_3{<}^{COOH}_{OH} \end{array} + C_6H_4{<}^{COOH}_{OH} + O$$



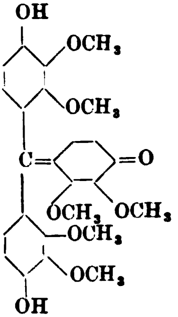
$$= H_2O + \begin{array}{l} C_6H_3{<}^{OH}_{COOH} \\ | \\ C{=}C_6H_3{<}^{O}_{COOH} \\ | \\ C_6H_3{<}^{COOH}_{OH} \end{array}$$

Any phenol, or substitution product of a phenol, may be substituted for the salicylic acid in this process.

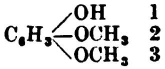
Later on, N. Caro (Ber. 25, 940) prepared a large number of carboxylated aurins by this process, substituting resorcylic, gallic, and cresotinic acid for the salicylic acid in the patented process. The compounds obtained proved to b very similar to chrome violet.

6. Of the large number of aurins prepare only one more need be mentioned here: **pittacal**, a curious substance discovered in 183 by Reichenbach in certain portions of beechwood tar. Liebermann more closely investigated this substance, and gave to it the name o *eupittonic acid* (Ber. 1876, 9, 334; 1878, 11, 1104). Hofmann determined its constitutio (*ibid.* 1878, 11, 1455; 1879, 12, 1371, 2261).

Pittacal is hexamethoxyaurin:

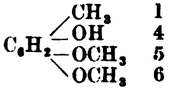


formed by the simultaneous oxidation of dimethylpyrogallol:



$$C_6H_3{<}\begin{array}{ll} OH & 1 \\ OCH_3 & 2 \\ OCH_3 & 3 \end{array}$$

and dimethyl methylpyrogallol:



$$C_6H_2{<}\begin{array}{ll} CH_3 & 1 \\ OH & 4 \\ OCH_3 & 5 \\ OCH_3 & 6 \end{array}$$

which are both contained in wood tar. The methyl group of the second compound yields the central carbon atom, the same as cresol did in the formation of the rosolic acid observed by Runge.

Pittacal is an orange substance, crystallising in beautiful crystals when pure. Its solution in caustic alkalis is of a beautiful blue colour.

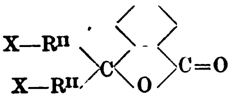
By heating pittacal with ammonia, Grätzel obtained a violet colouring matter, which proved of no practical value (*v.* Eupittonic Acid, vol. ii. 383).

III. The Phthaleïn Group.

The phthaleïns were discovered by Baeyer in his memorable researches on the condensation of phthalic acid with aromatic hydrocarbons and phenols. Their constitution was, however, at first misunderstood. In 1880, when the curious properties of phthalic anhydride became more definitely known, the error was corrected and the phthaleïns were recognised as congeners of the triphenylmethane group.

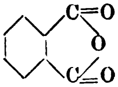
It is a well-known fact that every *o*-dicarboxylic acid is capable of forming, by losing the elements of water, an inner anhydride. These anhydrides act very easily on phenols, in some cases without the addition of condensing agents. Water is again eliminated, and a dye-stuff formed in every instance. Of the many colouring matters thus obtained, only those prepared from phthalic anhydride have, with one exception, become of general and practical interest, and these will here be described.

The central carbon in these dye-stuffs is afforded by one of the carbonyl groups of the anhydride of an *o*-dicarboxylic acid. If we restrict our consideration to phthalic anhydride, the formula may be thus modified :

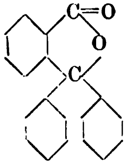


phthalic acid being benzene-*o*-dicarboxylic acid.

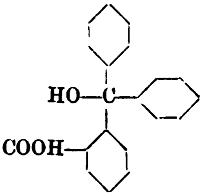
Phthalic anhydride, although perfectly symmetrical in its constitution



acts, in condensations, like an asymmetrical compound, only one of the carbonyl groups being attacked and losing its oxygen. Thus, by being condensed with two molecules of benzene it yields diphenyl phthalide or phthalophenone :



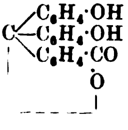
which is the parent substance of all the phthaleïns, just as triphenylmethane is the parent substance of the fuchsin and aurin groups. Diphenyl phthalide, however, is but the inner anhydride of triphenylcarbinol *o*-carboxylic acid :



hence the near relation between the phthaleïn, fuchsin, and aurin groups.

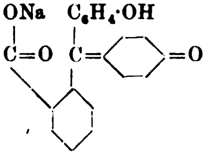
Formerly it was considered as probable that the anhydride structure of phthalophenone was preserved in the dye-stuffs derived from it. At present, almost all chemists are of the opinion that such is not the case, that the carboxyl group becomes free after the condensation has taken place and that it simply serves as a salt-forming group of minor importance. The quinonoid structure is shifted to the pyrone ring which is always present in all the really useful members of this group. Phenolphthaleïn and diaminophthalophenone, which do not contain the pyrone ring, are of no value as dye-stuffs. The constitution of the more important members of this group will be seen from the structural formulæ given for each of them.

1. **Phenolphthaleïn** $C_{20}H_{14}O_4$ was discovered by Baeyer in 1871 (Ber. 1871, 4, 658). Its constitution is



$$C\begin{cases} C_6H_4\cdot OH \\ C_6H_4\cdot OH \\ C_6H_4\cdot CO \\ \quad\; O \end{cases}$$

it may be considered as a substituted phthalophenone, but as in the free state it has no quinonoid structure, it is also colourless. It is easily prepared by heating phthalic anhydride with phenol in presence of sulphuric acid or stannic chloride. It forms pale-yellow crystals, which dissolve with a fine red colour in caustic alkalis. In the salt so formed the quinonoid structure is established and the substance thereby becomes a dye-stuff :



The practical importance of phenolphthaleïn is very small. Its only use is that of an indicator for alkalimetric purposes.

2. *Tetranitrophenolphthaleïn* $C_{20}H_{10}N_4O_{12}$ has been proposed as an orange colouring matter for wool. Its sodium salt $C_{20}H_8N_4O_{12}Na_2$ is sold as an orange powder under the name of *Aurotine*. It was discovered by C. Dreyfus, H. Bull, and T. Hall, and patented in England under 3441 (1889), in Germany under 52211. In a pure state free tetranitrophenolphthaleïn forms orange crystals, melting at 344°.

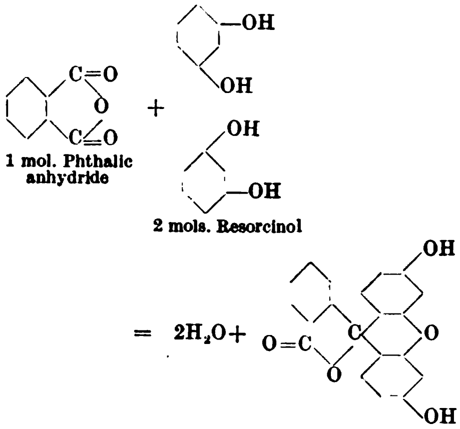
It has long been known that phenolphthaleïn is not a good dye. The same applies to all the ordinary typical phthaleïns. Phthalophenone (diphenylphthalide) is but a poor chromogen, but its properties are at once improved (as has already been shown above) if the two phenyl-radicles in its molecule be linked together by another group, preferably oxygen. We thus come to chromogens containing the pyrone ring combined with the structure of triphenylmethane derivatives, which, by the introduction of auxochromic groups, give rise to some of the most beautiful dye-stuffs yet discovered. As in all cases, the auxochromic groups introduced may be either the hydroxyl or the amino group ; and in the latter hydrogen may be replaced by organic radicles. We thus get phthaleïn colouring matters of either phenolic (acid) or aminic (basic) character. For a long time the former alone were known ; we will, therefore, consider them first.

A. *Acid phthaleïn dye-stuffs.*

The prototype of these is—

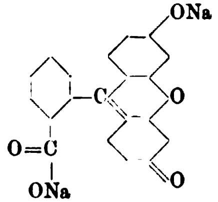
1. *Fluorescein* $C_{20}H_{12}O_5$. This beautiful substance is formed most easily if phthalic anhydride and resorcinol be mixed in molecular proportions and heated to 190°. In the factories this operation is carried out in enamelled cast-iron pots, heated in an oil bath. The ingredients melt, and large quantities of steam are given off. When the reaction is finished the mass solidifies into a cake of dark-brown colour, which consists of almost pure fluorescein.

In this reaction two molecules of resorcinol combine with one of phthalic anhydride. At the same time they interact upon one another, losing one molecule of water, and forming the pyrone ring :



Fluorescein

Fluorescein in a free state has thus a constitution quite analogous to that of phenolphthaleïn, although the presence of the pyrone ring is indicated by the intense brick-red colour of the substance. It is quite insoluble in water, sparingly so in the majority of other solvents. If, however, we dissolve it in alkaline liquids, it assumes, like phenolphthaleïn, its quinonoid nature and this change is marked by the intensity of its colour. In caustic alkalis and in ammonia it dissolves with a brown colour. The solutions have, especially when dilute, a most brilliant and beautiful green fluorescence. Hence the name of the substance.



Sodium salt of Fluorescein, showing quinonoid structure combined with pyrone ring

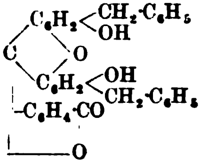
The crude fluorescein obtained in the manufacture, as above described, seems to contain two modifications of the substance (which may be isomerides). By treating the crude cake with boiling spirit, a certain amount of a soluble, non-crystallisable fluorescein is extracted, whilst the greater proportion of it remains undissolved, and is obtained as a crystalline residue on filtering. This process of purification is invariably used in the manufacture of the dye-stuff. Both the soluble and the insoluble part are worked up in the manner to be described hereafter, the insoluble fluorescein giving the better and purer qualities of the dye-stuffs, whilst the low-class qualities are made from the soluble fluorescein obtained by evaporating the alcoholic extract.

A small quantity of the fluorescein manufactured is transformed into its sodium salt

$$C_{20}H_{10}O_5Na_2,$$

which is sold, under the name *Uranin*, in the shape of a yellow powder, very soluble in water. It is used for dyeing pale yellows on silk.

If benzyl chloride and some sulphuric acid be added to the fluorescein melt a substance is obtained which is supposed to be benzyl-fluorescein :



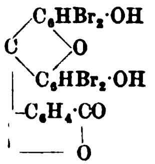
Its sodium salt is sold as a yellow dye-stuff under the name *Chrysolin*. This substance, discovered by Reverdin in 1877, is not of much practical importance.

By far the greater part of the fluorescein produced is transformed into very beautiful red colouring matters by the introduction of halogen atoms into its molecule. The dye-stuffs so prepared are known by the generic name of *Eosins*.

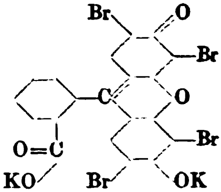
If fluorescein be treated by substituting reagents, it is generally observed that four atoms of hydrogen are replaced by other groups. Further investigations have shown that this substitution takes place in the phenyl radicles, which entered the fluorescein in the shape of resorcinol, whilst the phenyl radicle derived from the phthalic anhydride is never attacked by these reagents.

The most important of the dye-stuffs so prepared is

2. *Eosin* $C_{20}H_6O_5Br_4K_2$, the potassium salt of tetrabromofluorescein. The sodium salt is also occasionally met with, but it does not crystallise so well. The constitutional formula of eosin is :



(In a free state)



(As potassium salt)

Eosin is prepared by acting with four molecules of bromine upon one molecule of fluorescein. The crystallisable modification of the latter is used for the manufacture of a good product. On the small scale a solution of the fluorescein in glacial acetic acid is prepared, and the bromine introduced gradually.

For manufacturing purposes glacial acetic acid is too expensive. The following process, which admits of operating in aqueous solutions, may be used instead.

The bromine is dissolved in exactly the necessary quantity of caustic soda, and the solution is evaporated to dryness. The resulting salt consists of a mixture of sodium bromide and sodium bromate. It is dissolved in water and mixed with a solution of the theoretical quantity of fluorescein in caustic soda. The mixture is then acidified with hydrochloric acid. The bromine generated acts at once upon the fluorescein, and the precipitate obtained is eosin, which need only be dissolved in a solution of potassium carbonate and evaporated to crystallisation.

The quantity of bromine used may be reduced to half (two molecules or four atoms) by using a mixture of potassium bromide and potassium or sodium chlorate, instead of the salt obtained by evaporating the solution of bromine in caustic soda.

This process, although cheap and simple, is not generally used, because the bromine is found to act too energetically. A certain amount of the eosin is destroyed, and the remainder is not so brilliant in colour as it might be.

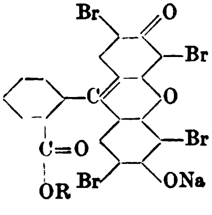
The bromination proceeds much better in an alcoholic solution; alcohol is, therefore, frequently used for the purpose in the manufacture of eosin. The fluorescein is finely ground, and suspended in strong spirit. The necessary quantity of bromine is added. The bromination takes place slowly and gradually, and an excellent product is obtained. The spirit is recovered by distillation.

In order to reduce the bromine in this as in the aqueous process to two instead of four molecules, the addition of a chlorate is necessary. But a chlorate must be used which is soluble in spirit. Cupric chlorate is preferred to any other. It is prepared by mixing concentrated aqueous solutions of sodium chlorate and cupric chloride or sulphate. The solution obtained is added to the operation in progress.

Eosin forms either a dark-brown powder, or dark-brown crystals with a green metallic lustre. The potassium salt may also be obtained in flesh-coloured crystals by re-crystallisation from spirit. These crystals contain alcohol of crystallisation. According to strength and purity of shade, the commercial eosins are distinguished by certain letters and additions, such as 'eosin B,' 'A,' 'GGF,' 'DH,' 'extra,' 'extra-fine,' 'soluble,' and others. All these brands dissolve easily in water, with a scarlet coloration. Dilute solutions show a marked greenish fluorescence.

Eosin is used for dyeing silk and other fibres, also for staining paper, and for preparing red inks of a very fine scarlet colour. Large quantities are used for the last-named purpose, Eosin is not a fast colour, but its brilliancy of shade secures a ready sale for the large quantities produced.

3. **Eosin soluble in spirit** (*Primrose, methyl-eosin*). These names are applied to certain products, which are produced by boiling eosin, dissolved in spirit, with caustic soda and methyl iodide, or ethyl bromide. The carboxyl group is thus alkylated, whilst the hydroxyl group remains combined with alkali. The sodium salts thus obtained form glistening crystals, insoluble in water but soluble in spirit. They have the constitution:



in which R stands for either methyl or ethyl. Small quantities of these substances are prepared and employed as an addition to the vermilion used in cotton printing, in order to increase the brilliancy of its shade. Spirit eosin was formerly also used for silk dyeing, but for this purpose it has been replaced by the bluish eosins soluble in water, to be described later on.

If the hydroxyl group of eosin is also to be alkylated, this can only be effected by acting with alkyl iodide or bromide upon the silver salt of eosin. The dialkyl-ethers thus obtained are colourless.

4. **Eosin scarlet** (*Eosin B, BN, BW, scarlet, J, JJ, V, &c.*). Sodium salt of dinitrodibromofluorescein $C_{20}H_6N_2O_9Br_2Na_2$.

If fluorescein be treated with nitric acid, dinitrofluorescein is obtained, which has found no application as a colouring matter. But by subsequent bromination it yields a brilliant scarlet. The same product (or an isomeride very similar to it) may be prepared by first brominating the fluorescein and then treating it with nitric acid.

This dye-stuff was hailed with enthusiasm when it made its appearance in 1875, but its use was soon much restricted by the introduction of the scarlet azo dyes which are quite as brilliant, and at the same time faster, cheaper, and more easy in their application.

5. **Erythrosin** (*Bluish Eosin, Dianthin, Primrose soluble, Pyrosin B,* and other names).

This is the sodium salt of tetraiodofluorescein $C_{20}H_6O_5I_4Na_2$. The potassium salt is also met with occasionally. It is prepared by iodinating fluorescein with iodine and oxidising agents, such as mercuric oxide, iodic acid, cupric chlorate, &c. It may also be prepared by introducing iodine monochloride into an alcoholic suspension of fluorescein.

Erythrosin dissolves in water, with a fine red colour, and very slight fluorescence. It dyes silk in shades which are much more bluish than those obtained with eosin.

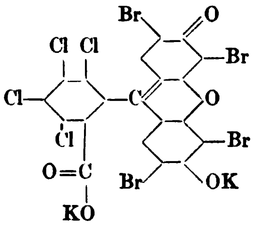
Erythrosin was introduced into the market in 1876 by Bindschedler and Busch. It was well received by the silk dyers. Owing to the high price of iodine, a mixture of eosin and Bengal red is now used for producing the same shades.

There is one application, however, for which pure erythrosin is still required—for producing orthochromatic dry plates for photographic purposes. As a sensitiser of silver bromide, erythrosin holds a prominent place amongst all the colouring matters hitherto tried.

Di-iodofluorescein was sold and used for a very short time as an orange dye-stuff, under the name '*Pyrosine J.*'

6. **Phloxin** (*Potassium salt of dichloro- or tetrachloro- tetrabromofluorescein*).

This colouring matter, discovered in 1876 by Nölting, together with the following ones, formed a new departure in the manufacture of the eosin dyes. The characteristic feature of these substances is the fact that they contain halogen atoms substituted for hydrogen, not only in the resorcinol groups, but also in the phenyl group derived from the phthalic anhydride. Now, it has already been said that a substitution of this kind cannot be effected in ready-made fluorescein. To prepare phloxin, therefore, or any of its congeners, a special fluorescein must be used, prepared not with ordinary phthalic anhydride but with the anhydrides of dichloro- or tetrachloro- phthalic acid. Dichlorophthalic acid is best prepared by oxidising dichloronaphthalene, whilst tetrachlorophthalic acid may be obtained by chlorinating phthalic anhydride in the presence of finely divided iron. Both acids give colouring matters of very similar shades, the tetrachloro derivatives being but very little bluer than the dichloro derivatives. The process of manufacture of the dye-stuffs is identical with that described for eosin. The constitutional formula of phloxin is



if derived from tetrachlorophthalic acid. The phloxin derived from dichlorophthalic acid contains, of course, two atoms of chlorine less.

Commercial phloxin is a red powder, soluble in water, with a red colour and no fluorescence. It dyes beautiful bluish-red shades on silk, which resemble those obtained with erythrosin.

7. **Cyanosin** is the monomethyl ether of phloxin. It is soluble in spirit, and dyes shades still bluer than phloxin.

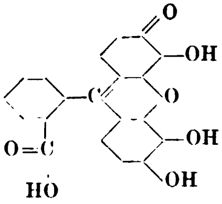
8. **Bengal red** (*Rose Bengale N*)

$C_{20}H_4Cl_2I_4O_5K_2$ or $C_{20}H_2Cl_4I_4O_5K_2$

is the iodo derivative of this series. It is the bluest eosin dye-stuff obtained. It is very expensive, and was formerly used in large quantities to produce the most brilliant bluish-reds on silk. It has now, to a great extent, been replaced by the rhodamines. Its methyl ether, soluble in spirit, received the name of *Cyanosin B*. Its application never became important.

The phthalein derivatives of resorcinol are all very brilliant dyes. There are, however, some other acid phthaleins which, although important as colouring matters, are of much more sober hues. They are derivatives of pyrogallol.

9. **Gallein** $C_{20}H_{12}O_7$. If phthalic anhydride be condensed with pyrogallol, the reaction takes place quite as easily as with resorcinol. The product obtained is, as might be expected, a dihydroxyfluorescein. The constitutional formula now adopted for gallein is



For the manufacture of gallein it is not necessary to prepare pure pyrogallol. Gallic acid may be used instead, which, losing carbon dioxide, is at once transformed into gallein by the action of the phthalic anhydride.

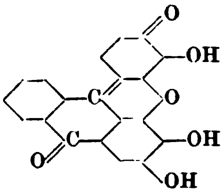
Gallein is generally sold in the shape of a violet paste. It is sparingly soluble in water, easily soluble in caustic alkalis, with a bright-blue coloration. It dyes mordanted wool and cotton. Chrome mordants are used preferably, and dark-violet shades are obtained.

On account of the similarity of the application of gallein to that of alizarin, gallein is also sold under the name of *Alizarin violet* or *Anthracene purple*.

10. **Cœrulein** (*Alizarin green, Anthracene green*) $C_{20}H_8O_6$. This is one of the most important dye-stuffs for wool and cotton, dyeing a beautiful and very fast olive green on chrome mordants. The cotton printer uses it constantly, both pure and mixed, with other dye-stuffs of the alizarin family.

It was discovered in 1871 by A. Baeyer, who obtained it by heating gallein with concentrated sulphuric acid to 200°. By the same process it is now prepared in immense quantities on the large scale.

In this process the substance loses one molecule of water and the carboxyl group forms a new hexagon ring by condensing with the neighbouring benzene ring, thus:



Cœrulein forms a black paste, insoluble in water. It is soluble in caustic alkalis, with a greenish-blue coloration.

11. **Cœrulein S** (*soluble cœrulein*)

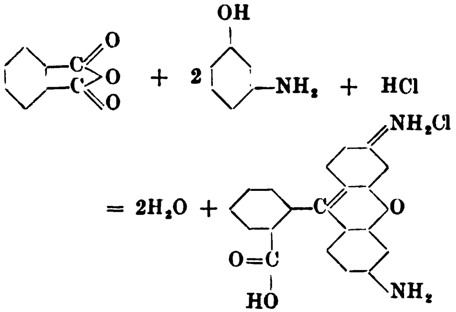
$C_{20}H_{10}O_{12}S_2Na_2$.

This is the product of the reaction of sodium bisulphite upon cœrulein; its manufacture is carried on by the Badische Aniline and Soda works at Ludwigshafen. It forms a black powder, soluble in water, with a brown coloration. It is easily decomposed by the addition of acids or by heat. It is used for the same purposes as cœrulein, and is very convenient, on account of its easy solubility. In dyeing with it, it is, of course, decomposed, the ordinary cœrulein being deposited on the fibre.

B. *Basic phthalein dye-stuffs.*

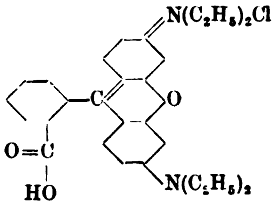
For a long time these were not known. The manner in which they might be obtained had, of course, suggested itself to the consideration of chemists, but the substances required for their synthesis seemed to be quite out of the reach of the manufacturer. In 1887, however, M. Ceresole, of the Badische Anilin- und Soda-Fabrik, successfully effected the synthesis of the first basic phthalein, which proved to be of such value that a thorough search for a good means of preparing the necessary ingredients was made, which led to complete success.

To obtain the basic substance analogous to fluorescein, it is merely necessary to replace one of the hydroxyl groups of resorcinol by an amino- group; or, in other words, to employ *m*-aminophenol instead of resorcinol:



Experience has shown that the compound thus obtained has no practical value. If, however, diethyl *m*-aminophenol is used instead of the *m*-aminophenol, a most beautiful colouring matter is obtained, known under the name of

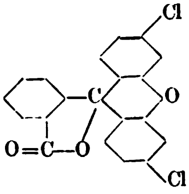
1. **Rhodamin B** $C_{28}H_{31}N_2O_3Cl$. The commercial product is the monohydrochloride :



It forms beautiful needles of a metallic green appearance, easily soluble in both water and spirit. Weak solutions show a most magnificent orange fluorescence, which disappears on heating, and reappears in the cold. This is the most beautiful red colouring matter ever prepared, dyeing silk, wool, and cotton a most brilliant pink of a bluish shade.

The process described for the production of rhodamin is patented by the Badische Anilin- und Soda-Fabrik, Eng. Pat. 15374, 1887; D. R. P. 44002. The diethyl *m*-aminophenol is prepared from diethylaniline by heating it with fuming sulphuric acid to 60°. diethylaniline *m*-sulphonic acid is formed, which yields the phenol by fusion with caustic soda.

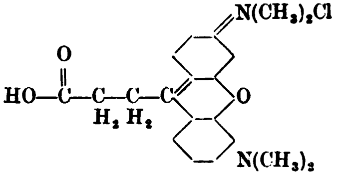
There is, however, another process for the manufacture of rhodamin, discovered by the Farbwerke of Höchst (D. R. P. 48367, 1888). It consists in treating free fluorescein with phosphorus pentachloride, when the fluorescein chloride



is formed. This is transformed into rhodamin if heated with diethylamine under pressure.

2. **Rhodamin S** $C_{20}H_{23}N_2O_3Cl$ and $C_{24}H_{31}N_2O_3Cl$.

These two colouring matters, which are identical in their practical properties and applications, are not, strictly speaking, triphenylmethane derivatives; nor are they derived from phthalic acid. They must, however, be mentioned here, because they are near congeners of rhodamin B. They are obtained by treating dimethyl- or diethyl- *m*-aminophenol, not with phthalic, but with succinic, anhydride. Succinic acid is the typical *o*-dicarboxylic acid of the fatty series. Like phthalic acid, it forms an anhydride, which condenses with resorcinol into fluorescein-like dye-stuffs; these, however, offer no practical interest. The succineines of dimethyl- and diethyl- *m*-aminophenol, however, show a sufficient difference from rhodamin to be manufactured and sold as a special brand. The constitution of the dimethyl compound may be represented by the following formula :



It is, therefore, not a triphenylmethane derivative. It is sold in the shape of its zinc double chloride.

Rhodamin S shows great affinity to unmordanted cotton. It is one of the few members of this group which may be considered to be what is now called a substantive colouring matter.

The properties of rhodamin S are very similar to those of rhodamin B. It forms crystals with a green metallic lustre, easily soluble in water, with a red coloration, and a marked yellow fluorescence. The shades obtained with it are yellower than those produced with rhodamin B.

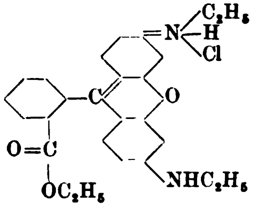
Rhodamin B and S remained for some time the only important members of this magnificent group of dye-stuffs. After a while, however, some new representatives of it made their appearance, of which the more important may be here shortly described.

Rhodamin G $C_{26}H_{27}N_2O_3Cl$ is obtained by heating rhodamin B with aniline hydrochloride. One of the ethyl groups is split off in the shape of ethyl chloride and the recovered dye-stuff is a tri-ethyl-rhodamin which dyes wool and silk in red shades of a much more yellowish tinge than the original rhodamin B.

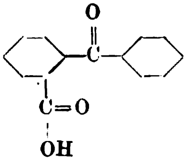
The process of alkylation, which produced such remarkable results in the eosin group, proved equally applicable to the rhodamins. It was carried out at first by using alkyl chlorides, but later on it was discovered that a much cheaper and simpler way to the same end consists in saturating alcoholic solutions of rhodamins with hydrogen chloride. As this is a method which is exclusively applicable to the alkylation of organic acids, the possibility of using it for the rhodamins formed a proof of the presence of a free carboxyl group in the dye-stuffs and went a long way in establishing the modern views about their constitution.

Rhodamin 3B, *Anisoline*, was the first of the alkylated rhodamins. It dyes a more bluish shade of red than rhodamin B, and is, if possible, even more brilliant and pure in its tinge, which strongly resembles that of certain flowers such as the 'Crimson Rambler' rose.

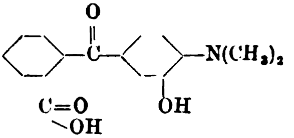
Rhodamin 6G was obtained by the same process from *sym*-diethylrhodamin (produced by the condensation of phthalic acid with two molecules of mono-ethyl-*m*-aminophenol), and has consequently the following constitution :



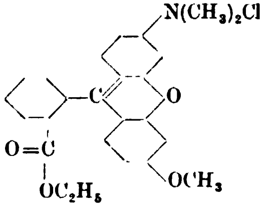
When once the constitution of the rhodamins was recognised, it was clearly seen that they may also be considered as derivatives of *o*-benzoyl-benzoic acid :



Suitable substitution products of this acid may therefore be used for the synthesis of rhodamins. This is important because it enables us to produce asymmetrical rhodamins, whilst the original process was applicable only to the production of symmetrical members of this important class of dye-stuffs. As an example of this method, *Rhodamin* 12 *GM* may be quoted, which is prepared by acting with dimethylhydroxybenzoylbenzoic acid :

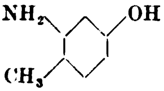


upon monomethylresorcinol and subsequent esterification of the product obtained. This dye-stuff is consequently quite asymmetrical and has the constitution :



It dyes silk, wool, and cotton a beautiful yellowish red.

If in the process given for the production of rhodamin 12 GM the monomethylresorcinol be replaced by *m*-amino-*p*-cresol :



a new and exceedingly beautiful dye-stuff is obtained, which is sold under the name *Irisamin G* or *Rhodin* 3*G*. It dyes silk, wool, and mordanted cotton a flaming, beautiful red.

Several other members of this group have been prepared by various methods, amongst which the reaction of formaldehyde upon ready formed rhodamins may be mentioned. All the rhodamins have also been found applicable not only to the regular dyeing of textile fabrics, but also to the staining processes so largely used for paper, wood and confectionery. Very large quantities of these dyes are used for such purposes.

Few groups of synthetical dye-stuffs have proved so prolific as that of which a short description has here been given. The triphenylmethane group contains some of the oldest artificial colouring matters known, but for more than half a century it has continued to yield new additions to the vast number of such compounds which chemical science has placed at the disposal of our textile industries. O. N. W.

TRIPHYLITE. A manganese lithium phosphate $LiMnPO_4$, occurring naturally as large, rough (orthorhombic) crystals and coarsely cleavable masses. By the isomorphous replacement of manganous oxide by ferrous oxide it passes into the closely allied mineral lithiophilite $(LiFePO)_4$. The colour is grey or bluish, but, the mineral being readily weathered, the masses are usually dark brown on the surface. Triphylite occurs in pegmatite-veins, often in association with spodumene and other lithium-bearing minerals, and sometimes with tin-ore. It is found at Bodenmais in Bavaria, Huréaux and Chanteloube in Haute-Vienne, Branchville in Connecticut, Pala in California, the Black Hills in South Dakota, and King's Mountain in North Carolina. Containing 8·1–9·4 p.c. of lithia it has occasionally been collected, when mining for other minerals, and used as a source of lithium salts. L. J. S.

TRIPOLITE or **TRIPOLI** *v.* KIESELGUHR.

TRÖGERITE *v.* URANIUM.

TROILITE. A name applied by Haidinger to ferrous sulphide FeS, occurring in meteorites.

TRONA, URAO, or **NATURAL SODA.** The sodium carbonates occurring as minerals are : thermonatrite Na_2CO_3,H_2O (orthorhombic) : natron (*q.v.*) $Na_2CO_3,10H_2O$ (monoclinic) ; trona $Na_2CO_3{\cdot}NaHCO_3,2H_2O$ (monoclinic) ; and possibly the anhydrous salt. Of these, trona is by far the most important and constitutes the larger part of the deposits of natural soda. It forms beds of white, cavernous material with acicular or bladed crystals lining the cavities ; and is usually intermixed with more or less earthy matter and sodium chloride and sulphate. It is deposited from the water of soda-lakes and forms an efflorescence on the surface in desert regions. The Natron Lakes of Lower Egypt are well known, and similar lakes and surface efflorescences of soda are met with in many parts of the Sahara and Sudan. Extensive deposits are found in the neighbourhood of Lake Chad, and a large deposit has been opened up at Lake Magadi in British East Africa. Soda-lakes also occur in the western states of North America, viz. in Arizona, California, and Nevada.

The name 'trona' is said to be of Arabic origin ; and 'urao' is a native name for the soda deposited at the bottom of a lake at Lagunilla in Venezuela.

References.—F. W. Clarke, Data of Geochemistry, Bull. U.S. Geol. Survey, No. 491, 1911; A. Lacroix, Minéralogie de la France et de ses Colonies, 1909, vol. iii. R. Wegscheider in C. Doelter's Handbuch der Mineralchemie, 1911, vol. i. 141–193. L. J. S.

TROOSTITE. A constituent of steel intermediate in characteristics between sorbite and martensite (*q.v.*). It is obtained by quenching highly heated steel in oil or by quenching from the transformation temperature in cold water, and is plentiful in tempered steels.

It acquires a deep brown or black tint when etched with picric acid, and can thus be distinguished under the microscope. Benedicks regards it as a colloidal solution of carbon in iron (J. Iron and Steel Inst. 1905, ii. 352; 1908, ii. 217). The name troostite is also given to a variety of *Willemite* (*q.v.*).

TROPACOCAINE *v.* SYNTHETIC DRUGS.

TROPAEOLINE *v.* AZO- COLOURING MATTERS.

TROPILLENE *v.* KETONES.

TRUFFLES, subterranean fungi, highly prized as food. Many species are known. König divides the edible truffles into two chief classes—

(1) **White truffles,** the best of which is the African truffle, *Tuber niveum* (Desf.) or *Terfezia Leonis* (Tul.), but also including the Italian truffle, *Tuber magnatum* (Pico.) or *Tuber album* (Balb.), with a garlic-like odour, and the German white truffle, *Tuber album* (Bull.) or *Chæromyces meandriformis* (Vitt.), of much less value.

(2) **Black truffles,** which include the highly prized French truffle *Tuber melanospermum* (Vitt.), which is usually in size between a walnut and an apple, of dark brown or black colour, and covered with polygonal warts. It possesses a strong aromatic odour, resembling that of the strawberry; the winter truffle, *T. brumale* (Vitt.) occurs in France and Italy, resembles the French truffle, but has not such an aromatic smell and taste. The summer truffle, *T. æstivum* (Vitt.) is the one most usually found in England, generally in beech, oak, or birch woods, and in marly soils. It is gathered from July to September.

König gives, as the mean composition of truffles—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
77·1	7·6	0·5	6·6	6·4	1·9

Chatin (Compt. rend. 1890, 110, 376, and 435) found the dry matter in French truffles to vary from 20·8 to 25·0 p.c. of the original fresh material, and to contain from 4 to 9 p.c. of its weight of nitrogen, and from 5·6–11·2 p.c. of ash. The ash, in different samples, contained: silica 10–35 p.c., potash 17–28, soda 0·6–2·1, lime 6·0–9·4, magnesia 0·2–3·1, ferric oxide and traces of alumina 3·2–8·4, manganous oxide, traces to 0·05, phosphorus pentoxide 18·4–30·2, sulphur trioxide 2·1–4·6, chlorine with traces of iodine 0·2–0·4 p.c. Much larger proportions of potash and phosphorus pentoxide were found in the ash of truffles by Kohlrausch and Loesecke, quoted by König. The amount of alumina is also apparently very variable, since Pizzi (quoted by König) found, in the ash of black truffles, 5·77 p.c. of alumina, in that of white truffles, 7·17 p.c.

As to the nature of the nitrogenous constituents of truffles, little appears to be known; probably a considerable proportion of it is in the non-proteid form.

In the non-nitrogenous extract, mannitol, trehalose and malic and citric acids have been found.

For an examination of the *tubulane* or Caucasian truffles, and of various species of *Terfezia*, known as 'terfas' and 'kames' in the north of Africa and in Western Asia *v.* Chatin (Compt. rend. 1893, 114, 46; and Revue intern. des falsific. 1893, 14).

Truffles are sold, either in the fresh condition, imbedded in lard, dried, or cooked and preserved in olive oil, or in hermetically sealed cases.

König gives, as the mean of 9 analyses of the air-dried product—

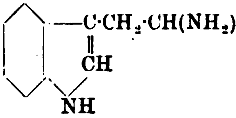
Water	Protein	Fat	N-free extract	Crude fibre	Ash
4·4	33·9	2·0	24·9	27·1	7·7

H. I.

TRYGASE *v.* SYNTHETIC DRUGS.

TRYPSIN *v.* FERMENTATION.

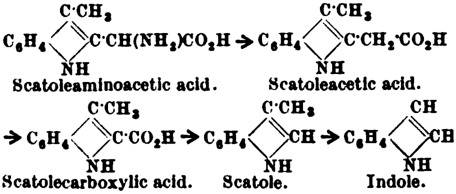
TRYPTOPHAN, *β-indole-α-aminopropionic acid*



It has been known since the researches of Gmelin, Barnard, and others of the earlier physiologists that on tryptic digestion a substance is formed from proteids that gives a reddish-violet coloration with chlorine or bromine. Other methods of decomposing proteids, such as putrefaction or alkali or acid hydrolysis, give rise to the same substance, for which the name *tryptophan* was suggested by Neumeister (Zeitsch. Biol. 1890, 26, 234), and *proteinchromogen* by Stadelmann (*ibid.* 491). The compound itself was not known until 1901 when Hopkins and Cole (J. Physiol. 1901, 27, 418) isolated it from the products formed by the tryptic digestion of casein; they showed that it possessed the formula $C_{11}H_{12}O_2N_2$, yielded scatole and indole when heated, and adopting Neumeister's suggestion named it *tryptophan.*

Tryptophan occurs among the products of hydrolysis of a large number of proteins, both of animal and vegetable origin (*v.* PROTEINS), and is separated by means of the sparingly soluble double salt it forms with mercuric sulphate. It is most conveniently prepared from casein or fibrin, the former yielding 7–8 grms. and the latter 13–14 grms. per kilo (Neuberg, Chem. Zentr. 1906, ii. 892; Neuberg and Popowski, Biochem. Zeitsch. 1906, 2, 357).

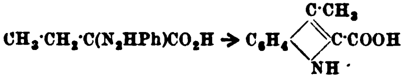
Constitution and synthesis. The formation of indole (Kühne, Ber. 1875, 8, 206; Nencki. *ibid.* 336), of scatole (Brieger, *ibid.* 1877, 10, 1027), of scatolecarboxylic acid (E. and H. Salkowski, *ibid.* 1880, 13, 2217) and of scatoleacetic acid (Nencki, Monatsh. 1889, 10, 506) on putrefaction of proteins was attributed by Nencki to the presence of a scatoleaminoacetic acid in the protein molecule; and when Hopkins and Cole found tryptophan to have the empirical formula $C_{11}H_{12}O_2N_2$ and to yield indole, scatole, scatolecarboxylic acid and scatoleacetic acid on putrefactive decomposition, they regarded their substance as Nencki's hypothetical scatoleaminoacetic acid



Scatoleaminoacetic acid. Scatoleacetic acid.

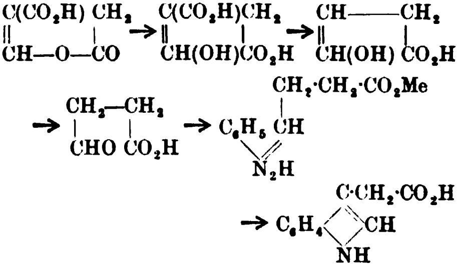
Scatolecarboxylic acid. Scatole. Indole.

Ellinger (Ber. 1904, 37, 1801), however, showed that Nencki's so-called scatolecarboxylic acid was not identical with the synthetic product obtained by Wislicenus and Arnold (*ibid.* 1887, 20, 3394) from the phenylhydrazine derivative of propionylformic acid



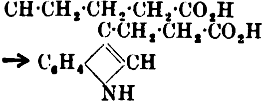
but was in reality the isomeric *indole acetic acid*

, obtained synthetically by condensing β-aldehydopropionic acid (obtained from aconic acid) with phenylhydrazine and subsequent treatment of the ester of the hydrazone with alcohol and sulphuric acid



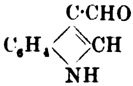
Ellinger (Ber. 1905, 38, 2884) further showed that Nencki's scatoleacetic acid was identical with indole propionic acid obtained by a similar synthetic process from ethyl propionacetalmalonate

$(CO_2Et)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OEt)_2$
$\rightarrow CH_2(CO_2H)CH_2{\cdot}CH_2{\cdot}CHO$
$\rightarrow C_6H_5{\cdot}N_2H : CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$

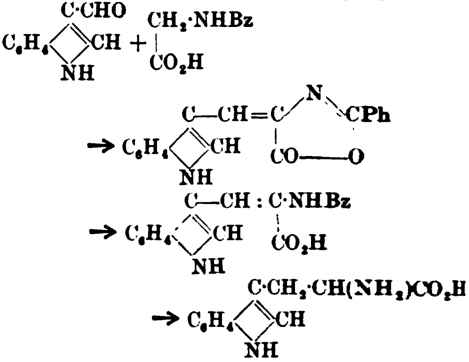


From these considerations it follows that tryptophan must be indole-3-α-aminopropionic acid or indole-3-β-aminopropionic acid, and that it possesses the constitution of the former compound was shown by Ellinger and Flamand (Ber. 1907, 40, 3029), who prepared it synthetically from indole-3-aldehyde and hippuric acid.

Indole-3-aldehyde



is obtained by oxidising tryptophan with ferric chloride (Hopkins and Cole, J. Physiol. 1903, 29, 451; Ellinger, Ber. 1906, 39, 2515), and can also be prepared by the action of chloroform and potassium hydroxide on indole; it condenses with hippuric acid to form an *azlactone*, which on hydrolysis yields *α-benzoylaminoindolylacrylic acid*. This compound on reduction and subsequent hydrolysis yields α-amino-β-indolepropionic acid, identical with *dl*-tryptophan



Properties. The tryptophan obtained from proteids is lævorotatory in aqueous solution. Hopkins and Cole (J. Physiol. 1901, 27, 418) found $[\alpha]_D -33°$, H. Fischer (Zeitsch. physiol. Chem. 1908, 55, 74) found $[\alpha]_D -34{\cdot}5°$ for one specimen, whilst others gave values varying from −29·75° to −40·3°; Abderhalden and Baumann (*ibid.* 412) found $[\alpha]_D^{20} -30{\cdot}33°$. In alkaline or acid solution, *l*-tryptophan is dextrorotatory, having $[\alpha]_D^{20} +5{\cdot}7°$ to $+6{\cdot}3°$ in a 2–3 p.c. solution in N/2NaOH solution, or +6·06° to +6·12° in 10–12 p.c. N/1 NaOH solution (Abderhalden and Kempe, *ibid.* 1907, 52, 207; Abderhalden and Baumann, *l.c.*); lower values were found by Fischer (*l.c.*), $[\alpha]_D +5{\cdot}56°$ to 5·69° in a 2–3 p.c. solution of a N/1 NaOH solution. This is probably due to partial racemisation as Abderhalden and Baumann (*l.c.*) found $[\alpha]_D^{20} +5{\cdot}27°$ for a specimen that had been repeatedly recrystallised; a 6 p.c. solution in N/1 hydrochloric acid gave $[\alpha]_D^{20} +1{\cdot}31°$ (Abderhalden and Kempe, *l.c.*). *l*-Tryptophan crystallises in six-sided and rhombic plates, is sparingly soluble in cold, readily so in hot water and has a slightly bitter taste; it darkens when heated at 240° and melts at 252° (Hopkins and Cole, *l.c.*), at 273° (Neuberg and Popowsky, *l.c.*), at 289° (corr.) (Abderhalden and Kempe, *l.c.*).

dl-Tryptophan is prepared synthetically and also readily formed from *l*-tryptophan which racemises on crystallisation from pyridine, or by the action of ammonia or by heating at 170° with hydrochloric acid (Abderhalden and Baumann, *l.c.*; Allers, Biochem. Zeitsch. 1907, 6, 272; Neuberg, *ibid.* 276); the racemic compound differs from the natural compound only in being optically inactive and in having a sweet taste. For the dissociation constants see Aristides Kanitz (Biochem. Zeitsch. 1910, 29, 126).

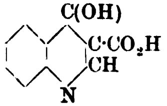
Reactions. The Adamkiewicz or Liebermann reaction given by certain proteins—namely, the formation of a blue violet ring at the junction of the two liquids when concentrated sulphuric acid is added to a mixture of the protein with acetic acid or ether—is due to the presence of tryptophan in the protein and of glyoxylic acid in the acetic acid or ether (Adamkiewicz, Ber. 1875, 8, 161; v. Liebermann, Zentr. Med. Wissensch. 1887, 321, 450; Hopkins and Cole, Proc. Roy. Soc. 1901, 68, 21; J. Physiol. 1901, 27, 418; Cole, J. Physiol. 1903, 30, 311; Osborne and Harris, J. Amer. Chem. Soc. 1903, 25, 853; Bardachzi, Zeitsch. physiol. Chem. 1906, 48, 145; Dakin, J. Biol. Chem. 1907, 2, 289). According to Homer (Proc. Camb. Phil. Soc. 1912, 16, 405), who has studied the behaviour of tryptophan towards certain aldehydes, it is formaldehyde rather than glyoxylic acid that is the substance essential to the formation of the characteristic violet colour in the Adamkiewicz reaction.

For other colour reactions of proteins due to the presence of tryptophan, see Cole (*l.c.*); Dakin (*l.c.*); Fleig (Proc. Soc. Biol. med. 1908, 65, 192); Rosenheim (Biochem. J. 1, 233); Granström (Beitr. Chem. Physiol. Path. 1908, 11, 132); Heimrod and Levene (Biochem. Zeitsch. 1910, 25, 18).

The red-violet colour produced by chlorine or bromine water on tryptophan is only given by free tryptophan, not by its polypeptides. The coloration attains a maximum when the amount of halogen is equivalent to four atoms per gram molecule of tryptophan, and when concentrated solutions are used red amorphous precipitates of the monohalogen derivatives are obtained $C_{11}H_{11}O_2N_2Cl$ and $C_{11}H_{11}O_2N_2Br$. These compounds are soluble in amyl alcohol, ether, or ethyl acetate, and the use of these solvents has been suggested to render the reaction more intense. The addition of excess of halogen converts the red compounds into yellow perhaloids $C_{11}H_{11}O_2N_2Cl_3$ and $C_{11}H_{11}O_2N_2Br_3$ (Neuberg and Popowski, Biochem. Zeitsch. 1907, 2, 357; Neuberg, *ibid.* 1910, 24, 423; Abderhalden and Kempe, *l.c.*).

Tryptophan is decomposed on heating into carbon dioxide, indole and scatole; when fused with potassium hydroxide, scatole, to the extent of 65 p.c. of the calculated amount, is the chief product (Hopkins and Cole, *l.c.*).

In the animal economy, tryptophan chiefly undergoes bacterial decomposition with the formation of indole; in the case of dogs it is partially converted into ***kynurenic acid*** (4-*hydroxyquinoline-3-carboxylic acid*)



(*v.* QUINOLINE) and excreted as such. The administration of tryptophan causes an increased excretion of kynurenic acid. The mechanism of the reaction whereby tryptophan undergoes conversion into kynurenic acid has not been explained (Kretschy, Ber. 1879, 12, 1673; Wein. Akad. Ber. 1881, 83, [ii.] 171; Monatsh. 1883, 4, 156; 5, 16; Solomin, Zeitsch. physiol. Chem. 1897, 23, 497; Capaldi, *ibid.* 1897, 23, 92; Mendel and Jackson, Amer. J. Physiol. 1898, 2, 1; Camps, Ber. 1901, 34, 2703; Mendel and Schneider, Proc. Amer. Physiol. Soc. 1900, ix–x; Amer. J. Physiol. 1901, 5, 427; Gies, *ibid.* 1901, 5, 191; Glaessner and Langstein, Beitr. chem. Physiol. Path. 1901, 1, 28; Ellinger, Ber. 1904, 37, 1801; Abderhalden, London and Pincussohn, Zeitsch. physiol. Chem. 1909, 62, 139).

Salts of l-*tryptophan.* *l*-Tryptophan has an acid reaction towards litmus, and forms salts both with acids and bases; the *copper salt* $(C_{11}H_{11}O_2N_2)_2Cu$, sparingly soluble grey-blue precipitate (Abderhalden and Kempe, Zeitsch. physiol. Chem. 1907, 52, 207); the *silver salt* $C_{11}H_{11}O_2N_2Ag$; the *sodium* salt has $[\alpha]_D + 2{\cdot}50°$ in 2 p.c. solution (H. Fischer, *l.c.*). The *hydrochloride* $C_{11}H_{12}O_2N_2{\cdot}HCl$ has m.p. 251° and $[\alpha]_D - 13{\cdot}44°$ in 2 p.c. aqueous solution (H. Fischer); the *picrate* $C_{11}H_{12}O_2N_2{\cdot}C_6H_3O_7N_3$ forms bright red lustrous needles or plates, m.p. 195°–196° (decomp.); the *picrolonate*

$$C_{11}H_{12}O_2N_2{\cdot}C_{10}H_8O_5N_4$$

forms orange red needles, m.p. 203°–204° (Mayeda, Zeitsch. physiol. Chem. 1907, 51, 261).

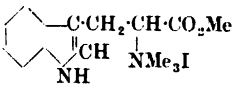
Esters and acyl derivatives. The *methyl ester* $C_{10}H_{11}N_2{\cdot}COOMe$ forms crystalline plates, m.p. 89·5° (corr.); the *hydrochloride*

$$C_{10}H_{11}N_2{\cdot}CO_2Me{\cdot}HCl$$

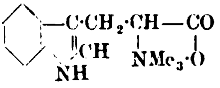
crystallises in microscopic needles, melts with decomposition at 214° (corr.); the *hydrochloride* of l-*tryptophanchloride* $C_{10}H_{11}H_2{\cdot}COCl{\cdot}HCl$ melts and decomposes at 228° (corr.) (Abderhalden and Kempe, *l.c.*). The *phenylcarbimide* derivative $C_{11}H_{11}O_2N_2{\cdot}CONHPh$ crystallises in needles, m.p. 166°; the *naphthylcarbimide* $C_{11}H_{11}O_2N_2{\cdot}CONH{\cdot}C_{10}H_7$, m.p. 159°–160°; the *benzenesulphonic derivative* $C_{11}H_{11}O_2N_2{\cdot}SO_2Ph$ melts and decomposes at 185° and forms a sparingly soluble sodium salt; the β-*naphthalenesulphonic* derivative $C_{11}H_{11}O_2N_2{\cdot}SO_2{\cdot}C_{10}H_7$ melts at 180°, the *sodium salt* at 304° (corr.) (Abderhalden and Kempe, *l.c.*; Ellinger and Flamand, Ber. 1907, 40, 3029).

Other derivatives of tryptophan are *monochlorotryptophan* $C_{11}H_{11}O_2N_2Cl$, an amorphous red precipitate, m.p. 280°, converted by excess of chlorine into the *perchloride* $C_{11}H_{11}O_2N_2Cl{\cdot}Cl_2$, a yellow precipitate decomposing at about 100°; *monobromotryptophan* $C_{11}H_{11}O_2N_2Br$, an amorphous red precipitate with a black reflex, m.p. 270°–280°; the *perbromide* $C_{11}H_{11}O_2N_2Br{\cdot}Br_2$ is yellow and decomposes at 75° (Neuberg and Popowsky, Biochem. Zeitsch. 1906, 2, 357).

The *betaine* of tryptophan is identical with the alkaloid *hypaphorine*, discovered by Greshoff (Mededeelingen uit's Lands Plantentuin, 1890, 7, 29) in the seeds of *Erythrina hypaphorus* (Boerl.). and is of considerable biochemical interest as it is the only naturally occurring simple derivative of tryptophan. The alkaloid can be synthesised from tryptophan by the action of methyl iodide, sodium hydroxide and methyl alcohol, which yields the *iodide* of *methyl-α-trimethylamino-β-indolepropionate*



m.p. 197°, and this on hydrolysis gives *hypaphorine* or *α-trimethylamino-β-indolepropiobetaine*



of which the *nitrate* has m.p. 215°–220° and

$[\alpha]_D+94{\cdot}7°$. Greshoff found $[\alpha]_D$ 91°–93° for the natural base (van Romburgh and Barger, Chem. Soc. Trans. 1911, 2068). M. A. W.

TSCHEN. Chinese coins of a brass or bronze-yellow colour, containing 55–64 p.c. copper, 26–35 p.c. zinc, and from 1–2 p.c. tin, 2–4 p.c. iron, and 1–6 p.c. lead; and occasionally small quantities of antimony, arsenic, and nickel (Pöpplein, Chem. Zentr. 1859, 484).

TSCHERMIGITE. Native ammonium-alum, first found at Tschermig in Bohemia.

TSCHEWKINITE $M''SiO_3M'''TiO_3$. A silicotitanate of iron, cerium, lanthanum, and didymium, of a velvet black colour, found in the Ilmen mountains.

TSE-HONG. A mixture of white lead, alumina, ferric oxide, and silica, used by the Chinese for painting on porcelain.

TSING-LIEN. A red pigment used in porcelain painting. Consists of a mixture of stannic and lead silicates with copper oxide or cobalt and gold.

TULA METAL. An alloy of silver, copper, and lead made at Tula in Russia.

TUNG OIL is obtained from the seeds of *Aleurites cordata* (Muell. Arg.) (*Elæococca cordata* [Bl.]; *Elæococca vernicea* [Juss.]; *E. sinensis* (*Dryandra vernicea* [Corr.]), trees indigenous to China and Japan. Trees belonging to the same species also grow abundantly in Indo-China, Tonkin, Annam, and Cambodja.

The fruits form a nut, in which three seeds, having a hard shell and an oleaginous kernel, are enclosed; hence in China the oil is frequently termed 'nut oil.'

The composition of tung oils varies somewhat according to their source, and the treatment of the seeds in different localities. Three kinds of seeds are distinguished—yellow, drab, and white. In China the seeds are roasted in a flat dish over a naked fire and then broken to powder between stones; finally the mass is expressed in crudely made wooden presses. The kernels contain about 53 p.c. of oil, but the yield of oil amounts to only 40–41 p.c. The cold-drawn oil is pale yellow, and termed white tung oil. This is the variety chiefly imported into Europe. The oil obtained by hot pressing is dark brown, and termed black tung oil. This oil is consumed at home; it has an unpleasant taste, and its odour is more pronounced than that of the white tung oil, which is also somewhat unpleasant. This odour precludes its use for many purposes. The objectionable smell is stated to be absent from oils obtained from seeds freed from all damaged kernels. Tung oil is also expressed in Madagascar, where the oil is known under the name 'Bakoly oil.' This name is most likely a corruption of 'bancoulier' (*Aleurites moluccana*). The Chinese and Japanese oils are not identical. They differ chiefly in their specific gravity (*see Characteristics* under Oils, Fixed, and Fats). The chief shipments of oil are made from Hankow and Wuchow in China; comparatively smaller quantities are exported from Japan (Hokkaido).

Tung oil is stated to consist chiefly of the glycerides of oleic and elæomargaric acids. Hence, although tung oil gives with the bromide test 0·38 p.c. of a precipitate, its fatty acids do not yield any ether-insoluble bromide. In the 'elaidin test' an oily layer is obtained resting on the lower, nearly solid product; when stirred up, the whole mass flows.

The oil is most readily identified by its strong characteristic smell, which it has hitherto not been possible to remove entirely.

The oil is further readily recognised by the manner in which it dries. It is frequently stated that tung oil is a better drying oil than linseed oil, inasmuch as it forms a skin more rapidly than does linseed oil; but the skin it yields, *e.g.* on a glass plate, although dry, is opaque, wax-like, and has no elasticity. Therefore, tung oil cannot replace linseed oil. Nevertheless, tung oil is now largely used as a substitute for linseed oil when the price of the latter is high. A number of patents have been taken out for the manufacture of boiled oils, varnishes, rubber substitutes, and linoleum, in which larger or smaller quantities of tung oil are used in place of linseed oil. *V.* Varnish.

A characteristic property of tung oil is to form a jelly on being heated to 250° for a short time, or even when kept at 180° for an hour or two. On exposure to the light the oil also becomes solid. The jelly-like mass so obtained possesses some elasticity, is insoluble in the ordinary solvents for oils, and shows no tendency to melt on again being heated to 250°. The gelatinisation is not due to oxygen absorption, since the conversion into a semi-solid mass takes place when air is carefully excluded. When heated with lead oxide or red lead, the oil gelatinises within 15 mins. to a light brown mass.

If a saturated solution of iodine in chloroform or any other solvent be dropped on tung oil, the oil is immediately solidified; and if the oil has been previously dissolved in chloroform, a jelly is obtained. Bromine has no such action on the oil.

Concentrated sulphuric acid gives a black clot with the oil. When 1 grm. of the oil is dissolved in 5 c.c. of chloroform, and 5 c.c. of a saturated solution of iodine in chloroform is added, and the mixture stirred, the whole is converted into a stiff jelly after about 2 mins. If 2 grms. of the oil be employed under the same conditions the jelly is so stiff that it can be granulated.

In China and Japan tung oil is used chiefly as a natural varnish for wood, for caulking junks and boats, as a common adulterant of lacquer, and also for lighting. Large quantities are also consumed for water-proofing paper and all kinds of tissues. The oil is further employed in admixture with powdered lime as a mortar. The best kinds of Chinese ink are obtained by burning the oil with a regulated amount of air. The cold-drawn oil is stated to be used in medicine as an emetic and also as a purgative. It should be noted that the raw oil is poisonous.

J. L.

TUNGSTEN. Sym. W. At.w. 184·0. Although found in most of the tin deposits throughout the world, the mineral *wolfram* which furnishes the bulk of the tungsten of commerce and its products, appears to have been regarded, until the middle of the eighteenth century, rather as a constituent of *cassiterite* than as an associated mineral. The term 'wolfram' was, in fact, apparently applied to it on account of its causing loss of tin in smelting, in the same sense that antimony was called 'the wolf' b the alchemist because it devoured the base metals when employed in the refining of gold.

In 1781, Scheele obtained a yellow powder (which he termed tungstic acid) by acid treatment of the aqueous extract from the fusion of a certain heavy lime mineral with potassium carbonate. The production of a yellow colouring matter by direct acid treatment of this mineral (afterwards termed *scheelite*), had been previously noted by Woulfe, who did not, however, explain its nature. Scheele's work was confirmed and amplified by Bergman in 1782, and the following year, his former pupils, the brothers D'Elhuyart, are stated to have shown the presence of tungstic acid in wolfram and to have produced metallic tungsten from it.

Although but little definite work was published on tungsten and its compounds prior to the nineteenth century, it is evident that a considerable amount of knowledge existed, and an interesting short note in Nicholson's journal for 1801, states that Guyton had melted tungsten, but that it was brittle and probably useless except in alloys or for making fixed colours or 'fixing' vegetable colours—three of its present uses. The earliest recognised commercial uses of tungsten ores were, in fact, for the production of sodium tungstate for fireproofing purposes or as a mordant, &c., for the preparation of tungstic acid and other coloured compounds suitable for use as pigments, &c., and for the manufacture of alloys.

As regards the use of tungsten for hardening steel, it is curious that the old Damascus steel, always celebrated for its retention of temper, has been found to contain both tungsten and chromium, although probably not intentionally added. The patents of Mushet (1859) for the manufacture of steel, &c., containing tungsten, following a patent by Oxland (1857) for the production of certain alloys of tungsten with iron and steel, nickel, &c., and the earlier and more important patent of Oxland (1847) for the manufacture of sodium tungstate, tungstic acid and metallic tungsten from tin-wolfram ores, may be considered to form the basis of all present commercial methods of treating tungsten ores and of practically all the technical uses of the metal and its compounds.

Like many other rare heavy metals, tungsten occurs mainly in minerals found in the oldest plutonic rocks and in the alluvium produced by their denudation, a large proportion being obtained in the form of a wolfram concentrate during the dressing of tin ores.

Tungsten is an essential constituent of a considerable number of minerals but, commercially speaking, may be said to be only produced from wolfram and scheelite. The term 'wolfram' or 'wolframite' should, mineralogically, be confined to the tungstate of iron and manganese $FeWO_4 \cdot MnWO_4$, theoretically containing 76·47 p.c. of tungstic acid or 60·7 p.c. of tungsten, but the minerals *ferberite* $FeWO_4$, and *hübnerite* $MnWO_4$, which contain almost the same proportion of tungstic acid as true wolfram, are commonly included under the generic name 'wolfram' for market purposes. The iron and manganese contents of both are, in fact, so variable that it is often difficult to say under which class a so-called 'wolfram' should be placed. No specimen of hübnerite free from iron, or of ferberite free from manganese, has yet been found.

Scheelite $CaWO_4$ (theoretically containing 80·55 p.c. of WO_3) is also an important tungsten mineral, but its common association with rare metals (molybdenum, &c.) and base metals (antimony, &c.), from which it is difficult to effect a separation, has resulted in a smaller output and a lower price as compared with wolfram. Among other minerals may be mentioned *reinite*, a variety of ferberite, $FeWO_4$, *cupro-scheelite* $CaWO_4 \cdot CuWO_4$, *stolzite* or *raspite* $PbWO_4$, and *wolfram ochre* WO_3. The last-named mineral is commonly found as an incrustation produced by the weathering of tungsten minerals, but occasionally occurs massive, and the author has an interesting piece which was sent to England as scheelite, but is almost pure tungstic acid, apparently of colloidal origin.

The principal localities where tungsten minerals are found are England (Cornwall), Spain, Portugal, Bohemia, Saxony, Bolivia, Peru and Argentina, the United States, Canada, the Malay States, Australasia, Nigeria, and South and East Africa. The largest producers are the United States (mainly Colorado) and the Commonwealth of Australia, which respectively produced 1821 and 1789 short tons (2000 lbs.) in 1910, the world's production in that year being estimated at 6950 short tons. These figures have been calculated from the tungstic acid contents reported, on the assumption that the ore, as sold, averaged 60 p.c. of WO_3.

Although their value mainly depends on the amount of tungsten which they contain, at least 90 p.c. of the output being absorbed in the manufacture of the metal and its alloys, the minerals of tungsten are invariably sold on the basis of their tungstic acid content. The best concentrated or hand-picked material contains from 70 to 74 p.c. WO_3, but the usual value of that sold in bulk varies between 60 and 70 p.c., the latter being considered of exceptionally good quality. Material even lower than 60 p.c. is saleable, but is penalised for the impurities. Although the sale of wolfram is commonly a matter of private treaty, schedules covering ores of various percentages and showing the limits allowed for phosphorus, sulphur and other impurities, are published by several firms in the United States, and the demand is increasing more rapidly than the supply.

The composition of selected specimens of the principal tungsten minerals of the nature of wolfram, is shown in the following table compiled from various sources, including Dr. W. F. Hillebrand of the United States Geological Survey and H. E. Wood of the Colorado Scientific Society:

	Wolfram		Ferberite			Hübnerite
	Colorado	Zinnwald	Harz	Spokane	Colorado	Colorado
	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.
WO_3 .	74·10	75·99	76·25	75·0	75·9	75·58
FeO .	11·07	9·62	20·20	18·0	23·0	0·24
MnO .	14·35	13·96	3·96	3·0	0·6	23·40

The analyses are all those of picked specimens, any silica, lime, alumina and other gangue material being ignored. Traces of columbium, tantalum, and other rare metals, as well as of tin and copper, are commonly present in actual combination, even in selected crystals.

Wolfram ore is commonly separated from the gangue by wet dressings but, as any other heavy minerals which may be present in the original material also accumulate in the concentrate, it is usually necessary to carry out a further dressing. Owing to the high price of wolfram, the cost of such treatment is usually justified, especially when tin ore is associated with the wolfram, which is penalised for the presence of tin if more than 2 or 3 p.c. of that metal is present. The usual method of separating wolfram from other minerals in the concentrate, depends on the fact that it is slightly magnetic, and consists in the use of an electro-magnetic separator. Such treatment has proved the salvation of many tin mines, by dividing a concentrate previously almost unsaleable, into two products, tin ore and wolfram, each of which commands a good price in the market. The treatment usually produces four products, one which is valueless (magnetic iron ore, &c.) but the removal of which increases the value of the remainder, a fairly clean wolfram product, an intermediate product known as 'middlings' or 'tinny wolfram,' and a fairly clean tin concentrate ready for sale to the tin smelters. The losses, both in wet dressing to produce the original rough concentrate, and in the magnetic separation, are heavy, especially in the case of reef ore, which constitutes the bulk of the supply and which frequently contains less than 1 p.c. of wolfram and seldom exceeds 5 or 6 p.c.

The treatment of tungsten ores for the manufacture of metallic tungsten or of its oxides or salts, comprises a series of operations which, although chemically and metallurgically simple, require extreme care and experience and, even under the best conditions, result in heavy losses. It is true that ferro-tungsten is now being increasingly made by direct reduction of the ore in the electric furnace, and that the old difficulty, due to the large proportion of carbon formerly always present in directly made ferro-tungsten, has been largely overcome, but metallic tungsten and its alloys are still mainly prepared by the reduction of tungstic acid prepared from sodium tungstate which has been obtained by fusion of wolfram with sodium carbonate.

The 'Oxland' process, patented in 1847 and still used with practically no modification, for the manufacture of sodium tungstate from wolfram ores or from mixtures of wolfram and 'black tin' or cassiterite, consists in heating a mixture of the powdered ore with about 10 p.c. more than the theoretical amount of sodium carbonate (often with the addition of about 10 p.c. of sodium nitrate), in a reverberatory furnace at a red heat. The charge is occasionally stirred and the temperature is regulated so that the mass does not fuse but can be drawn out in a pasty condition when (after about four hours) the reaction is completed. The use of sodium sulphate instead of carbonate was proposed by Oxland but results in irregularity in the furnacing and in the nature of the product, and has met with no general application. The charge is leached with water in superimposed vats in which the weak liquors from the final washing of one charge can be used for the first extraction of another. The solution is crystallised and re-crystallised for the preparation of the pure tungstate, or is evaporated to dryness for the crude salt. The principal impurities in the tungstate thus prepared are sodium sulphate, silicate and arsenate, together with traces of iron and manganese, apparently present as ferrate and manganate. The iron, manganese and arsenic may be precipitated by the addition of a small quantity of caustic soda, whilst the bulk of the sodium sulphate crystallises out prior to the crystallisation of the tungstate and most of the silicate remains in the mother liquor from the tungstate crystals. Hence, almost chemically pure tungstate can be obtained by re-crystallisation, even from the crudest tungstate. Some difficulty is introduced when the wolfram is highly silicious, *i.e.* when it has not been carefully dressed, on account of the tendency towards the formation of silico-tungstates, but their presence merely means the retention of a large proportion of tungstate in the mother liquor, and there is a considerable demand (for fire-proofing purposes, &c.) for the crude salt obtained by evaporation of the liquor to dryness. The tungsten is, however, often precipitated as the calcium salt by addition of milk of lime or calcium chloride, the calcium tungstate thus obtained being afterwards converted into tungstic acid by treatment with hydrochloric acid. The residue from the leaching consists essentially of the oxides of iron and manganese, and is useful as flux in smelting operations. When the wolfram employed was admixed with 'black-tin,' as is commonly the case, the residue is dressed on shaking or other tables and the black-tin separated for sale to the tin smelters.

For the manufacture of tungstic acid, the second step in the production of metallic tungsten, a boiling solution of sodium tungstate is poured into boiling hydrochloric acid diluted with its own bulk of water, the granular tungstic acid thus obtained being filtered and washed in presses. The strength of the solution of both tungstate and acid and the method of admixture, stirring, filtering and washing, require the most careful supervision, and under the best conditions both temporary and permanent losses are heavy, partly from the production of a soluble acid tungstate and partly from the formation of colloidal tungstic acid, both of which pass through the filter or dissolve during the washing. The production of both is minimised by the use of excess of acid, by adding the tungstate to the acid slowly, with constant agitation and at the highest possible temperature and by washing rapidly with dilute acid. The necessity for thorough washing is accentuated by the fact that the retention of a very small proportion of sodium tungstate results in the production of a greenish tinge in the dried tungstic acid, which is supposed to be then less suitable for the preparation of metallic tungsten powder.

The third and last step in the manufacture of tungsten consists in the reduction of tungstic acid by heating in crucibles with carbon, or by reduction at a red heat in producer gas, hydrogen or other reducing gas. The reduction in gas results in the production of the purest metal, but is difficult to control or complete, so that the simpler crucible process is mainly employed. Slightly less than the proportion of carbon theoretically required for the reduction of the metal with production of carbon monoxide is employed, and it is usual to wash the metal and thus remove the free carbon together with the finer particles of tungsten metal and undecomposed oxide. The fine-grained but distinctly granular residual metal is sold, while the amorphous and extremely fine particles which have been washed off are mixed with the next charge for reduction.

Notwithstanding the readiness with which tungsten powder oxidises, it is still mainly used in preference to the fused metal obtained by the alumino-thermic method or in the electric furnace, or to ferro-tungsten obtained by direct reduction from the ore. On account of its high melting-point, it dissolves more readily in steel when added in the form of powder, and its heavier cost in that form is more than counterbalanced by its greater purity, although it is probable that fused tungsten or ferro-tungsten of the necessary purity will shortly be commercially available and will be employed on an increasing scale.

Metallic tungsten may also be prepared by the direct reduction of sodium tungstate with carbon at a heat sufficient to volatilise the sodium which is simultaneously produced, or by similarly reducing calcium tungstate and dissolving out the lime which remains with the resultant powdered metal. The metal obtained by this and many other apparently simple processes is, however, always impure, and the only commercial methods known consist in the reduction of tungstic acid by the processes already referred to. Tungsten powder, as sold to the steel makers, usually contains over 98 p.c. of tungsten together with about 0·5 p.c. each of iron and silicon, under 0·5 p.c. of carbon (commonly 0·1 or 0·2 p.c.) and practically no sulphur or phosphorus. The manufacturing costs, and the losses in each stage of the treatment, are so heavy that, apart from the cost of the ore, the value of the metal ultimately obtained is higher than might be expected. It is found that, although 100 parts of tungsten is theoretically obtained from about 127 parts of tungstic acid, an amount of wolfram containing over 140 parts is required to yield that amount of metal. The costs or 'returning charges' per ton of metal are commonly taken at £80, so that when wolfram ore, containing 60 to 65 p.c. of tungstic acid, sells at about £100 per ton, tungsten powder will command about £300.

Although readily obtained in the massive state in the electric furnace, Moissan found that it could only be produced free from carbon if the heat was not allowed to actually melt it, and although the objection to the presence of carbon is less in the case of steel-making—the principal use of the metal—tungsten or ferro-tungsten containing as much as 1 or 2 p.c. of carbon finds only a limited outlet. High-speed, self-hardening tools, for the manufacture of which the bulk of the tungsten is employed, sometimes contain as much as 10 or even 20 p.c. of tungsten and must be free from more than a small, definite amount of carbon, so that the use of high carbon tungsten or alloy would be impossible. The method now employed for the manufacture of pure tungsten for sheet or wire is not fully known, but is stated to depend upon a final refining *in vacuô* of the purest metal obtainable by reduction of the oxide with carbon. Carbon and occluded gases are removed and, as in the case of tantalum, a metal is obtained which has properties entirely different from those of ordinary so-called pure tungsten.

Tungsten is ordinarily obtained as a powdered or semi-fused, crystalline, brittle metal, harder than glass and having a sp.gr. of between 16 and 17. That obtained by Moissan in the electric furnace had a sp.gr. of 18·7 and was softer than glass. The properties of pure wrought tungsten are entirely different from those of the powdered or ordinary cast metal. It is white, lustrous, tough and non-magnetic, and can be rolled, like steel, into thin sheet, welded at a yellow heat and drawn into wire considerably thinner than one-thousandth of an inch. It melts at about 3000° (3002° according to recent determinations made with the optical pyrometer at the Wisconsin University). Its tensile strength increases as the drawing proceeds. Wire of 5 mm. diameter (*i.e.* $\frac{1}{1000}$ inch) has a tensile strength in pounds per square inch, of 460,000, while that of 1·2 mm. rises to 580,000, hard drawn piano wire of 3 mm. having a tensile strength of 507,000 lbs. The sp.gr. of the pure wrought metal is 18·81, and slightly more when the metal is drawn into wire. It is stated to be as high as 18·92 when heated to 1000° and compressed at 200 atmospheres. Hard drawn tungsten wire has an electrical resistivity of 6·2 microhms per centimetre cube at 25°, the temperature co-efficient for 0° to 170° being 0·0051. The corresponding figure for annealed wire is 5·0.

Tungsten is unaffected by water or air at ordinary temperatures, but both air and steam oxidise it at a red heat. Molten sulphur or phosphorus attack it slowly, while at a red heat their vapours rapidly convert it into the sulphide or phosphide. It does not combine directly with nitrogen. It is readily attacked by fused oxidising salts, such as alkaline nitrates and peroxides. Fused bi-sulphates and alkalis or alkaline carbonates also attack it, but their solutions have no action. At ordinary temperatures, bromine, iodine and sulphuretted hydrogen do not affect it, but chlorine has a slight and sodium hypochlorite a considerable solvent action. Strong or weak hydrochloric acid has no action upon it at ordinary temperatures, but the strong acid slowly attacks it at the boiling-point and produces a coating of black oxide. Boiling dilute sulphuric acid has no action, but the hot strong acid attacks it slowly. Concentrated nitric acid has but little action, but the dilute acid produces a yellow coating of tungstic acid which, as is also the case with *aqua regia*, appears to practically prevent further action. Hydrofluoric acid does not affect the metal, even when hot, but attacks it rapidly when mixed with nitric acid.

There is reason to think that a considerable future use for this metal lies in the manufacture of laboratory and other utensils, as, although not so resistant to certain reagents as platinum or tantalum, there are many purposes for which its special resistance to such reagents, coupled with its greater cheapness, will render it of special value.

Although the production of tungsten minerals may not appear at first sight to justify the statement that tungsten is one of the most important metals other than those commonly spoken of as commercial metals, the saving which has been introduced by its employment in steel manufacture and in the electric-light industry, shows very remarkable figures. In the case of the electric-light industry, in which the use of tungsten has only come into prominence within the last six years (the use of drawn tungsten wire only within about three years), the figures are particularly interesting. Although the actual amount of metallic tungsten used for filament lamps at the present time is measured only in pounds or hundredweights, it is estimated in the Mineral Resources of the United States for 1910 that, assuming the present lamp consumption to require 80 million 25 watt tungsten lamps per annum, the saving in current effected by employing tungsten lamps in place of the old carbon filament lamps would result in an annual saving of between £40,000,000 and £50,000,000 per annum. Economies far greater than the present or any possible saving in electric lighting are effected in engineering work through the use of tungsten for the manufacture of what are commonly called self-hardening lathe tools, drills, &c., which retain their temper even at a red heat, and are practically the only ones now employed in the larger works. Although the value of Mushet steel has been known for over fifty years, it is only within the last twenty years that tungsten steel can be said to have been largely used, but it is stated that Sheffield alone now uses between 1000 and 1500 tons of tungsten powder annually in its manufacture.

Tungsten combines directly with carbon, silicon and boron at or near the melting-point, and may be alloyed with many metals although but few alloys are at present in use. The alloys may commonly be prepared at a considerably lower temperature than the melting-point of tungsten, as it dissolves in other molten metal, the main precaution necessary being the use of a suitable flux to prevent access of air which rapidly oxidises powdered tungsten at the temperatures employed.

Although powdered metal is mainly employed direct in the manufacture of alloys, ferro-tungsten, and tungsten alloys with nickel, chromium and manganese as well as silico-tungsten, are also prepared for use in steel-making or for the production of special tungsten alloys.

Apart from steel-making, which accounts for over 90 p.c. of the metal, tungsten alloys of extremely varied composition are in use or have been suggested for many purposes, including wires for electrical resistances, bronzes, &c., but, although tungsten can be alloyed with most metals, the cost of the alloy is commonly altogether out of proportion to its value.

The following table shows the composition of a number of typical varieties of tungsten powder and ferro-tungsten as employed on the large scale, the former as prepared by reduction of tungstic acid with carbon, and the latter as obtained in the electric furnace :

	Tungsten powder		Ferro-tungsten		
	1	2	1	2	3
W	97·02	98·63	85·15	79·43	71·80
Fe	0·61	0·59	14·12	18·60	24·35
C	0·32	0·12	0·45	1·49	2·58
Si	0·72	0·32	0·13	0·16	0·36
Mn	0·16	—	0·085	0·21	0·78
P	nil	—	0·018	0·017	0·008
S	nil	—	0·021	0·016	0·02
Al	0·47	0·21	—	0·001	0·07
Cu	—	—	—	—	0·008
Mg	0·32	—	—	—	—

The principal salts and other compounds of tungsten are described under a separate heading. Although of great theoretical interest, there are few to which any commercial use can be applied, only the yellow oxide WO_3, and the tungstates of the alkalis or alkaline earths being employed as such or as steps in the production of the metal.

C. T. H.

Compounds of Tungsten.

Oxides. Tungsten is said to form a number of oxides the separate existence of which is not definitely settled. Thus, when sulphuric acid acts on metallic tungsten under varying conditions, the blue oxides, WO, W_2O_3, W_4O_3, W_5O_9, are formed ; sulphurous acid acts on tungsten forming the oxide W_5O_{14}, and a beautiful purple oxide with a yellow metallic lustre, W_3O_5, is obtained by heating ammonium metatungstate to a bright red heat or by fusing tungstic acid with potassium iodide (Desi, J. Amer. Chem. Soc. 1897, 19, 213).

The **hydroxide** W_5O_{14},H_2O, a dark blue powder with a purple lustre, is formed when tungstic acid is reduced with stannous chloride and hydrochloric acid, or by heating the acid with hydrogen iodide in a sealed tube at 200°. With ammonia it yields ammonium tungstate and the hydroxide W_3O_8,H_2O (Allen and Gottschalk, Amer. Chem. J. 1902, 27, 328).

The only oxides which are definitely known are WO_2, W_2O_3, WO_3.

Tungsten dioxide WO_2 may be prepared by the reduction of the trioxide or an alkaline metatungstate with zinc and hydrochloric acid (Pfordten, Ber. 1883, 16, 508) or by heating the trioxide to a dull redness in hydrogen (Riche, Ann. Chim. Phys. 1857, [iii.] 50, 29 ; Greenwood, Chem. Soc. Trans. 1908, 1493). It may be obtained crystalline by reducing lithium paratungstate with hydrogen (Hallopeau, Compt. rend. 1898, 127, 512).

Tungsten dioxide may be formed by heating an intimate mixture of tungsten trioxide and $\frac{1}{5}$–$\frac{1}{10}$ its weight of glycerol, ethylene glycol or similar hydroxyl compound, to a bright red heat for some hours (Eng. Pat. 18922, 1907 ; J. Soc. Chem. Ind. 1908, 22).

Tungsten dioxide, prepared in the wet way is of a copper red colour, prepared in the dry way it is a brown powder. It is readily oxidised to the trioxide ; heated in chlorine it yields a yellow oxychloride WO_2Cl_2. When amorphous it is soluble in hydrochloric and in sulphuric acid, but is quite unacted on when crystalline.

Blue tungstic oxide W_2O_3, formed when tungsten trioxide is reduced with hydrogen at 250°–300° (Malaguti, Compt. rend. 1835, 1, 292) or by electrolysing fused sodium tungstate

(Smith, Ber. 1880, 13, 753), is readily oxidised to the trioxide.

Tungsten trioxide (*tungstic oxide or anhydride*) WO_3 occurs naturally as *wolframine* and as *tungstite* or *meymacite* (Walker, Amer. J. Sci. 1908, [iv.] 25, 305), also in the form of tungstates in *wolfram* and *scheelite*. It may be prepared by calcining in contact with air, the lower oxides, the metal, a sulphide or its hydrate (tungstic acid), *v.* below.

Tungsten trioxide forms a yellow powder which may be obtained crystalline by heating the amorphous metal to a very high temperature in air or by fusion of tungstic acid with borax in a porcelain vessel (Nordenskjöld, Pogg. Ann. 1861, 114, 612); or by passing hydrogen chloride over tungstic acid or a mixture of sodium tungstate and sodium carbonate at a white heat (Debray, Compt. rend. 1862, 55, 287). Its sp.gr., when amorphous, varies between 5·27–7·13, when crystalline between 6·30–6·38. It is fusible with difficulty and is insoluble in water. When heated in hydrogen it gives the blue oxide at 250°, the dioxide at a red heat, and the metal if the latter action is prolonged. It is also reduced when heated with zinc and certain other metals (Delépine, Bull. Soc. chim. 1900, [iii.] 23, 675). When heated with chlorine or sulphur monochloride, it is converted into a volatile oxychloride and in the former case also into the hexachloride (Smith and Fleck, J. Amer. Chem. Soc. 1899, 21, 1008; Bourion, Compt. rend. 1908, 146, 1102; Defacqz, *ibid.* 1319).

The oxide is soluble in hydrofluoric acid, but not in hydrochloric or nitric acids or in *aqua regia*. *See* also Ehrenfeld, J. Amer. Chem. Soc. 1895, 17, 381).

Plastic masses of tungsten oxide for incandescent lamp filaments may be prepared by treating the oxide or hydrated tungstic acid with ammonia at −20° or below, or when in alcoholic suspension with gaseous ammonia (Eng. Pat. 14850; J. Soc. Chem. Ind. 1908, 1198, 1104).

Tungstic acids. Tungsten trioxide forms two well characterised acids, WO_3,H_2O or H_2WO_4 and $(WO_3)_4H_2O$ or $H_2W_4O_{13}$. In addition the salts of a number of polytungstic acids are known (Schaefer, Zeitsch. anorg. Chem. 1903, 38, 142).

Tungstic acid H_2WO_4 may be obtained by precipitating a solution of a tungstate with excess of hot acid. If cold acid is used, the white *hydrate* H_2WO_4,H_2O is formed, from which the acid may be obtained by boiling. It is prepared by digesting a tungsten mineral with hydrochloric acid, then with *aqua regia* until the brown powder has become yellow, when the iron and manganese have been dissolved out. The residue is well washed and then shaken with ammonia which dissolves the free tungstic acid. On filtration and evaporation the tungstic acid crystallises out. The finely powdered mineral may be fused with calcium chloride or with alkali carbonates or sodium chloride. The melt is lixiviated and the calcium or other metallic tungstate residue is then decomposed with nitric or hydrochloric acid.

Tungstic acid may be prepared from wolfram or other mineral containing tungsten, by heating the mineral under pressure with a concentrated solution of potassium hydroxide, lime or baryta being added to form insoluble compounds with some of the impurities.

The tungstic acid is then separated from the solution either by fractional precipitation with acid, the impurities separating first, or the whole of the precipitate formed by adding sufficient acid is fractionally redissolved by alkali. The process is said to be economical, convenient, and to give very pure acid (Fr. Pat. 389040, 1908; J. Soc. Chem. Ind. 1908, 939).

Tungstic acid may be purified by treating tungsten trioxide with carbon tetrachloride vapour at a red heat. The resulting volatile chlorine compound is sublimed, condensed and treated with *aqua regia*; the tungstic acid formed is then further purified by solution in ammonia and reprecipitation with dilute nitric acid (U. S. Pat. 926084; J. Soc. Chem. Ind. 1909, 794).

Tungstic acid is a yellow powder insoluble in water and almost so in all acids except hydrofluoric acid, in which it dissolves to the extent of 44·7 p.c. at 25°, 55·3 at 50°, using 50 p.c. hydrofluoric acid (Rosenheim and Bernhardi-Grisson, 7th Inter. Congr. Appl. Chem. 1911, Sect. x. 120). It is readily soluble in alkalis.

Freshly prepared tungstic acid dissolves in aqueous solutions of most aliphatic amines forming substituted ammonium tungstates such as $(NMeH_3)_6W_7O_{24},6H_2O$, which crystallise on evaporation. When heated they are decomposed forming the amine, tungstic acid and the blue oxide of tungsten (Ekeley, J. Amer. Chem. Soc. 1909, 31, 664). It also gives crystalline precipitates with pyridine and quinoline (Rosenheim and Bernhardi-Grisson, *l.c.*).

Colloidal tungstic acid may be prepared by adding hydrochloric acid to concentrated sodium tungstate solution until it has an acid reaction. The white gelatinous precipitate formed, protected from currents of air, is washed by decantation several times at 0° to 5°: 15 parts of the acid are then dissolved in 1 part of concentrated oxalic acid by gently warming, and the liquid is subjected to dialysis. If the outer water is changed frequently, the oxalic acid may be completely removed (Pappadà, Gazz. chim. ital. 1902, 32, ii. 22; see Sabanéeff, Zeitsch. anorg. Chem. 1897, 14, 354).

Colloidal tungstic acid may be obtained by dissolving 5 grms. of tungsten tetrachloride in about 50 c.c. of a mixture containing equal volumes of ethyl alcohol and ether; the filtered solution is diluted to 250 c.c. with alcohol and then mixed with an equal volume of water. The colloidal solution thus obtained behaves as a positive colloid; it may be kept for some days without appreciable opalescence being observed, but coagulation occurs more quickly by adding a larger quantity of water, and immediately when small quantities of neutral salts, hydroxides, or strong acids are added. Weak organic acids or rise in temperature exert no effect. If an electric current is passed through, a deep blue precipitate separates at the cathode (Müller, Zeitsch. Chem. Ind. Kolloide, 1911, 8, 93; Lottermoser, Verh. Ges. deut. Naturforsch. Aerzte, 1910, 11, 70; Wöhler and Engels, Koll. Chem. Beihefte, 1910, 1, 454; Zeitsch. Elektrochem. 1910, 16, 693).

The colloidal acid is also prepared by dialysing a 5 p.c. solution of sodium tungstate to which sufficient hydrochloric acid has been added to combine with the sodium. Colloidal tungstic acid forms a gum-like mass which may be heated at 200° without becoming insoluble and which at a red heat is converted into the trioxide. The colloidal acid has, probably, the constitution of the *meta* acid.

Tungstic acid and sodium tungstate are used in the production of colour resists for aniline black. 200 grms. sodium tungstate dissolved in 1 litre of gum tragacanth paste constitutes a white resist which may be rendered more lustrous and opaque by passing the printed tissue, after steaming, through a solution of barium chloride. The compound thus formed may be coloured by pigments, such as vermilion, ultramarine blue and chrome green, a series of pale resist colours being formed, along with which the usual albumin and tannic acid colour mixtures may be printed (Scheurer, Bull. Soc. Ind. Mulhouse, 1900, 138; *ibid.* 1898, 122).

Tungstic acid may also be employed in the production of resist effects upon *p*-nitraniline red and of discharge effects upon indigo-dyed tissues. In the latter case, the tissue dyed with the indigo is padded in a solution of sodium tungstate, dried and printed with a steam discharge mixture containing barium chlorate, potassium ferrocyanide and a basic dyestuff able to withstand the oxidising action, such as rhodamine 6 G, ultramarine, or chrome yellow. The colours are rendered faster by the addition of albumin together with an alkali citrate or tartrate.

Metatungstic acid $H_2W_4O_{13},7H_2O$, first isolated by Scheibler (J. pr. Chem. 1861, [i.] 83, 310), may be prepared by decomposing the lead salt with hydrogen sulphide or the barium salt with dilute sulphuric acid. It crystallises in small yellow octahedra, very soluble in water, giving a bitter solution, and loses its water of crystallisation at 100°. For its behaviour on electrolysis see Leiser (Zeitsch. Elektrochem. 1907, 13, 690).

Paratungstic acid, the acid corresponding to the salts of the formula $12WO_3,5M_2O,Aq$, has been prepared in dilute solution by mixing barium paratungstate with a quantity of dilute sulphuric acid not quite sufficient for complete decomposition. The solution cannot be concentrated even *in vacuô* without decomposition, and when boiled it yields tungstic acid (Hallopeau, Compt. rend. 1895, 121, 61).

Tungstates. The alkaline tungstates

$$M_2WO_4Aq$$

are prepared by fusing a naturally occurring tungstate with sodium or potassium hydroxide or carbonate, preferably with the addition of a silicious or other flux. The alkali tungstate falls to the bottom and may be tapped off, or, after cooling, the slag may be removed (J. Soc. Chem. Ind. 1885, 116; *ibid.* 1900, 542; *ibid.* 1899, 171; Eng. Pats. 30053, 1897; 6045, 1900).

The *sodium salt* crystallises in thin prisms, soluble in 4 parts of cold, in 2 parts of hot water, the solution having a bitter taste and an alkaline reaction. It has m.p. 698° (Parravano, Gazz. chim. ital. 1909, 39, ii. 55).

The *potassium* salt forms large prismatic crystals. The ammonium salt is very unstable.

Calcium tungstate $CaWO_4$ occurs native as *scheelite* and may be prepared artificially by the interaction of calcium chloride and a normal tungstate. If the amorphous white precipitate so obtained is mixed with lime and heated in a current of hydrogen chloride, it is obtained crystalline. The corresponding *barium tungstate* was prepared by Rousseau for use instead of white lead (Schoen, J. Soc. Chem. Ind. 1900, 740).

Lead tungstate occurs native as *stolzite* and crystallises in red tetragonal pyramids.

Ferrous tungstate occurs as *wolfram*

$$(FeMn)WO_4$$

forming dark grey or brownish-black prisms.

Manganese tungstate is found as *hübnerite*. Granger (Compt. rend. 1898, 127, 106; *ibid.* 1905, 140, 935) has proposed the employment of the tungstates in the ceramic industry.

Ammonio copper tungstate $CuWO_4,4NH_3$, deep blue crystals, are readily decomposed. A similar zinc salt is also known (Briggs, Chem. Soc. Trans. 1904, 675).

The copper compound

$$CuO,4WO_3,6NH_3,8H_2O,$$

has been obtained by the interaction of an ammoniacal solution of copper sulphate and ammonium tungstate. It forms small blue needles (Briggs, *loc. cit.*).

Sodium paratungstate $Na_{10}W_{12}O_{41},Aq$ is known commercially as tungstate of soda and may be prepared on a large scale by roasting wolfram with soda ash and lixiviating the fused mass. The boiling solution is then nearly neutralised with hydrochloric acid and allowed to crystallise when large triclinic crystals of the salt separate. It is sometimes used as a mordant instead of sodium stannate in dyeing and calico printing. It also renders cotton, linen, &c., non-inflammable. The corresponding potassium salt is formed in glistening scales when normal potassium tungstate is boiled with a little water.

For various paratungstates see Hallopeau, Ann. Chim. Phys. 1900, vii. 19, 92; Taylor, J. Amer. Chem. Soc. 1902, 24, 629.

Metatungstates $M'_2W_4O_{13},Aq$ were discovered by Margueritte (Ann. Chim. Phys. 1846, [iii.] 17, 475). The alkali salts are readily formed when the normal tungstates are boiled with tungstic acid until the filtrate no longer gives a precipitate on addition of hydrochloric acid. The other metatungstates are best prepared by double decomposition of the barium salt with the required sulphate or carbonate. The metatungstates have a bitter taste, are generally readily soluble in water and deposit tungstic acid on prolonged boiling. A large number of them are known but there is considerable difference of opinion as to their constitution (Copaux, Compt. rend. 1909, 148, 633; Zeitsch. anorg. Chem. 1911, 70, 297; Rosenheim, *ibid.* 418; *ibid.* 1911, 69, 247; Just, Ber. 1903, 36, 3619).

Pertungstates $M'WO_4,Aq$ are formed by boiling a paratungstate with hydrogen peroxide (Péchard, Compt. rend. 1891, 112, 1060); or by electrolysing a slightly acid solution of sodium tungstate (Thomas, J. Amer. Chem. Soc. 1899, 21, 373). More highly oxidised compounds are formed by treating the pertungstates with hydrogen peroxide (Melikoff and Pissarjewsky, Ber. 1898, 31, 632; Pissarjewsky, J. Russ. Phys. Chem. Soc. 1902, 34, 472).

Tungsten bronzes are compounds of the alkali metals with tungsten and oxygen, which, owing to their colour and insolubility in acids and alkalis have been employed as substitutes for bronze powders. Their exact constitution is not known, although they are generally regarded as compounds of the tungstates with tungsten dioxide. They may be obtained by the reduction of the tungstates heated to redness with hydrogen, coal gas, zinc, iron or tin.

Tungsten bronzes may be prepared electrolytically by fusing tungstic acid with the calculated amount of metallic carbonate and electrolysing the mass. A series of brightly coloured mixed alkali and alkaline earth tungsten bronzes of various compositions are described by Engels (Zeitsch. anorg. Chem. 1903, 37, 125) and Schäffer (*ibid.* 1904, 38, 148).

Four *tungsten sodium bronzes* are known, $Na_5W_6O_{18}$ of a golden yellow colour, $Na_2W_5O_{15}$ of a blue colour, $Na_2W_3O_9$ of a purple red colour, and $Na_4W_5O_{15}$ which forms red-yellow cubes and yields a brown-yellow powder (Philipp, Ber. 1882, 15, 499).

Potassium forms one bronze, $K_2W_4O_{12}$ (Knorre and Schäffer, *ibid.* 1902, 35, 3407).

Blue lithium bronzes are described by Hallopeau (Compt. rend. 1898, 127, 512).

Tungstates of the rare earths are described by Hitchcock (J. Amer. Chem. Soc. 1895, 17, 483).

TUNGSTEN AND THE HALOGENS.

Tungsten hexachloride WCl_6 is prepared by heating metallic tungsten in excess of pure dry chlorine, particular care being taken to exclude all traces of air and moisture in order to avoid the formation of the oxychloride (Roscoe, Annalen, 1872, 162, 349). A small quantity of the latter is formed at the beginning of the reaction, however, in spite of all precautions. It should be driven off beyond the portion of the tube where the chloride is to be collected. Tungsten hexachloride forms dark violet opaque crystals, which are very stable when pure but are readily decomposed by moist air or water, if the slightest trace of the oxychloride is present. It has m.p. 275°, b.p. 346·7°/759·5 mm.

Tungsten pentachloride WCl_5 is formed by the incomplete reduction of the hexachloride in a current of hydrogen. It is volatile and when redistilled forms long, pure black shining crystals, m.p. 248°, b.p. 275·6°. It is hygroscopic and dissolves in water forming an olive-green solution, but most of it decomposes into the blue oxide and hydrochloric acid (Roscoe, *l.c.*).

Tungsten tetrachloride WCl_4 forms the non-volatile residue in the production of the pentachloride. It may also be prepared by the distillation of the latter or of the hexachloride, or better, a mixture of the two chlorides in a current of hydrogen. It forms a greyish-brown crystalline powder (Roscoe, *l.c.*). It is hygroscopic, infusible, is partially decomposed by water and is reduced by hydrogen to the metal.

Tungsten dichloride WCl_2 is best prepared by heating the tetrachloride in a current of carbon dioxide at the temperature of a moderately hot zinc bath. It is a grey non-volatile powder partly decomposed and partly dissolved by water forming a brown solution (Roscoe, *l.c.*).

Tungsten dioxydichloride WO_2Cl_2, obtained by passing chlorine over the dioxide, forms light lemon-yellow scales. Heated with ammonia it forms the compound $W_4O_4N_4H_2$ (Smith and Shinn, Zeitsch. anorg. Chem. 1893, 4, 381).

Tungsten oxytetrachloride, beautiful red needle-shaped crystals, m.p. 210·4°, b.p. 227·5°, is formed by the interaction of the trioxide and phosphorus pentachloride (Schiff, Annalen, 1879, 197, 185); or by passing the vapour of the hexachloride over the heated trioxide.

Tungsten hexabromide WBr_6 obtained by heating tungsten with dry bromine vapour in an atmosphere of nitrogen, forms blue-black needles which decompose when heated to a high temperature, give a colourless solution in aqueous ammonia, fume in air and give a royal blue oxide when treated with water (Schaeffer and Smith, J. Amer. Chem. Soc. 1897, 18, 1098).

Tungsten pentabromide, prepared by passing dry hydrogen bromide over tungsten hexachloride at 300°, or better by the action of excess of bromine on tungsten, forms fern-like aggregates of dark needles with green reflex, m.p. 276°, b.p. 333°. It is very hygroscopic, yields the blue oxide when treated with water and dilute acids and is decomposed by alkalis, alkali nitrates, carbonates and bisulphates (Defacqz, Ann. Chim. Phys. 1901, [vii.] 22, 247).

Tungsten oxybromides WO_2Br_2, $WOBr_4$ and the compounds WCl_3Br_3, WCl_6, $3WBr_6$ are also known (Defacqz, Compt. rend. 1899, 129, 515).

Tungsten tetriodide WI_4, obtained by the action of an excess of liquid hydrogen iodide on tungsten hexachloride at 110°, is a black crystalline substance of sp.gr. 5·2 at 18°, decomposed by water, alkali-hydroxides and carbonates. Soluble in absolute alcohol (Defacqz, Compt. rend. 1898, 127, 510).

Tungsten diiodide WI_2, obtained by the action of hydrogen iodide on tungsten hexachloride at 400°, is an amorphous, insoluble, infusible, non-volatile brown powder of sp.gr. 6·9 at 18° (Defacqz, *ibid.* 1898, 126, 962).

Tungsten hexafluoride WF_6 may be obtained by the interaction of tungsten hexachloride with anhydrous hydrofluoric acid or with arsenic trifluoride, or, best of all, antimony pentafluoride. It has m.p. 2·5° and b.p. 19·5°. Is readily soluble in alkalis, attacks glass and most metals and forms double salts with alkali fluorides. When acted on by water it yields tungstic acid (Ruff, Zeitsch. anorg. Chem. 1907, 52, 256).

Tungsten oxytetrafluoride WOF_4, obtained by the interaction of the oxytetrachloride and anhydrous hydrogen fluoride, forms small colourless hygroscopic plates, m.p. 110°, b.p. 185°–190°, is decomposed by water forming tungstic acid and absorbs large quantities of ammonia in the cold (Ruff, *l.c.*).

Tungsten dioxydifluoride is known in an impure state. For various double fluorides see Marignac (Ann. Chim. Phys. 1863, [iii.] 69, 63); Marchetti (Zeitsch. anorg. Chem. 1895, 10, 66); Miolati and Rossi (Real. Accad. Lincei. 1896, [v.] 5, ii. 223); Ephraim and Heymann (Ber. 1909, 42, 4456).

TUNGSTEN AND SULPHUR.

Tungsten disulphide WS_2 may be prepared by passing hydrogen sulphide over tungsten hexachloride at 375°–550°, or by fusing an intimate mixture of pure dry potassium carbonate, flowers of sulphur and tungsten trioxide. It is a grey-black crystalline powder, insoluble in water, fairly stable, and has sp.gr. 7·5 at 10° (Defacqz, Compt. rend. 1899, 128, 609).

Tungsten trisulphide WS_3, best obtained by treating a sulphotungstate with excess of acid, is a brown powder which becomes black when dried, is slightly soluble in cold water, more so in hot water, and readily in alkali hydroxides and carbonates (Corleis, Annalen, 1885, 232, 244). It has been obtained in the colloidal state by Winssinger (Bull. Assoc. Sci. Belg. 1888, 15, 390).

The compounds, $WCl_6,3WS_3$ (Ann. Chim. Phys. 1901, [vii.] 22, 238) and WO_2S (Winssinger, *l.c.*) and a number of metallic sulpho- or thiotungstates, M_2WS_4 (Corleis, *l.c.*), have been described. A *di-* and *tri-selenide* (Uelsmann, J. 1860, 92) and a *tritelluride* are also known.

Tungsten nitrides W_3N_2, W_2N_3, a number of oxynitrides, nitretamido and oxynitretamido compounds, and also a hydroxylamine tungstate have been obtained (Wöhler, Annalen, 1850, 73, 190; *ibid.* 1858, 105, 258; Rideal, Chem. Soc. Trans. 1889, 41; Wöhler, *ibid.* 1851, 3, 171; Desi, *l.c.*; Allen and Gottschalk, *l.c.*).

TUNGSTEN AND PHOSPHORUS.

Tungsten combines directly with phosphorus when heated to redness, forming a dark green *phosphide* W_3P_4.

Tungsten diphosphide WP_2 produced by heating tungsten hexachloride at 450° in a current of hydrogen phosphide forms a black crystalline mass insoluble in water, sp.gr. 5·8. The phosphorus is readily displaced by the halogens and by sulphur and nitrogen at high temperatures. It may be reduced by heating with hydrogen, zinc or copper (Defacqz, Compt. rend. 1900, 130, 915).

If tungsten diphosphide is heated with a large excess of copper phosphide in a graphite crucible in a wind furnace and the product treated with dilute nitric acid, it yields the *monophosphide* WP, grey lustrous prismatic crystals, sp.gr. 8·5 (Defacqz, *ibid.* 1901, 132, 32).

Another *phosphide* W_2P is formed by reducing a mixture of phosphorus pentoxide (2 mols.) and tungsten trioxide (1 mol.) in a charcoal crucible at a high temperature (Wöhler, Chem. Soc. Trans. 1853, 5, 94).

Phosphotungstic acid. Tungstic acid combines with phosphoric and also with arsenic, antimonic and vanadic acids to form complex compounds of varying composition, $M_2O_5:WO_3 = 1:7$ to $1:24$ analogous to the molybdates. Phosphotungstic acid is used as a reagent for the precipitation of alkaloids, proteins and some of their products of hydrolysis, also for the detection of potassium and ammonium salts with which it gives insoluble precipitates. It may be prepared by acidifying a solution of 4 parts of sodium tungstate and 1 part of sodium phosphate with sulphuric acid and extracting the phosphotungstic acid with ether (Winterstein, Chem. Zeit. 1898, 22, 539).

Literature on phosphotungstic acids and the phosphotungstates (Kehrmann, Zeitsch. anorg. Chem. 1891, 1, 428; Soboleff, *ibid.* 1896, 12, 16; Rogers, J. Amer. Chem. Soc. 1903, 25, 298).

Tungsten arsenide WAs_2, prepared by heating tungsten hexachloride in a current of hydrogen arsenide at 150°–360°, is a black crystalline insoluble powder of sp.gr. 6·9 at 18°.

Tungsten chloroarsenide W_2AsCl_9, obtained by heating the above substances in a sealed tube at 60°–70°, forms hygroscopic bluish-black crystals, decomposed by water and acids (Defacqz, Compt. rend. 1901, 132, 138).

For *arsenictungstic acids* and *tungstates* see Kehrmann and Rüttimann (Zeitsch. anorg. Chem. 1899, 22, 285). *Vanadotungstates* (Friedheim, *ibid.* 1894, 6, 11; Rogers, *l.c.*; Friedheim and Henderson, Ber. 1902, 35, 3242). *Antimoniotungstates* (Hallopeau, Compt. rend. 1896, 123, 1065). *Zirconotungstates* (*ibid.* 1896, 122, 1419). *Alumino-* and *alumino-phospho-* and *arseno tungstates* (Daniels, J. Amer. Chem. Soc. 1908, 30, 1846).

Tungsten boride WB_2, prepared by fusing the two elements together in an electric furnace, crystallises in hard octahedra, sp.gr. 9·6 (Tucker and Moody, Chem. Soc. Trans. 1902, 16).

TUNGSTEN AND CARBON.

When tungsten trioxide is fused with calcium carbide in an electric furnace, it forms an iron-grey *carbide*, CW_2, which is harder than corundum and has sp.gr. 16·06 at 18°. In the presence of a large excess of iron, the *carbide* CW, an iron-grey crystalline powder of sp.gr. 15·7 at 18°, is formed (Moissan, Compt. rend. 1897, 125, 839; Williams, *ibid.* 1898, 126, 1722).

Chromium tungsten carbide $CW_2,3C_2Cr_3$ is formed by heating a mixture of chromic oxide, tungstic acid and carbon in a carbon crucible in an electric furnace for five minutes with a current of 400 ampères at 75 volts and treating the product with warm hydrochloric acid, then with concentrated ammonia solution. It forms small hard stable crystalline grains of sp.gr. 8·41 at 22°. By the addition of tungsten to chromium steels, the formation of this stable hard carbide might give rise to the production of new steels with special qualities (Moissan and Kouznetzow, Compt. rend. 1903, 137, 292).

Iron tungsten carbide $3W_2C,2Fe_3C$, a magnetic substance, sp.gr. 13·4 at 18°, has also been prepared (Williams, *ibid.* 1898, 127, 410; Carnot and Goutal, *ibid.* 1899, 128, 207).

TUNGSTEN AND SILICON.

Tungsten silicide WSi_2 has been prepared by heating copper silicide with amorphous tungsten in an electric furnace, using a current of 800–900 ampères and 50 volts, the resulting product is then washed successively with nitric acid, caustic potash, warm hydrofluoric acid and water. It may also be prepared by reducing a mixture of silica and tungstic anhydride with sulphur and alumina. It forms brilliant, grey crystals, of sp.gr. 9·4, which are not magnetic and are very stable (Defacqz, Compt. rend. 1907, 144, 848; Hönigschmidt, Monatsh. 1907, 28, 1017).

The **silicide** W_2Si_3 is obtained by heating the trioxide with silicon in the electric furnace, after which the mass is suspended in dilute hydrochloric acid (1 in 10) and electrolysed. The excess of metal dissolves and the silicide is removed, washed with *aqua regia*, then with ammonia, and is finally separated from carbon silicide gravimetrically by suspension in methyl iodide

(Vigouroux, Compt. rend. 1898, 127, 393). It forms beautiful steel grey crystals with a metallic lustre, sp.gr. 10·9. *See* also Frilley, Rev. de Metallurgie, 1911, 8, 457; J. Soc. Chem. Ind. 1911, 1018.

Tungsten aluminium silicide forms black hexagonal crystals (Manchot and Kieser, Annalen, 1904, 337, 360).

Silicotungstic acids of the formulæ,

$$H_8W_{10}SiO_{36},3H_2O,$$

$H_4W_{12}SiO_{42},20H_2O$, $H_8W_{12}SiO_{42},29H_2O$, &c., were discovered by Marignac (Ann. Chim. Phys. 1864, [iv.] 3, 5). The acid corresponding to the last formula is formed by precipitating its salts with mercurous nitrate and decomposing the mercury salt with hot hydrochloric acid. It crystallises in large tetragonal prisms, is readily soluble in water, alcohol, and ether, and forms a valuable reagent for alkaloids. The salts, most of which are soluble in water, are prepared by boiling gelatinous silicic acid with metallic polytungstates (Wyrouboff, Bull. Soc. franc. Min. 1896, 19, 219; Friedheim and Henderson, *l.c.*).

ORGANIC SALTS OF TUNGSTEN.

Esters of tungstic acid are described by Smith and Dugan (J. Amer. Chem. Soc. 1899, 21, 1016); *alkali tungsten tartrates* by Henderson and Barr (Chem. Soc. Trans. 1896, 1456); *citrates* by Henderson, Orr and Whitehead (*ibid.* 1899, 547); *tungsten oxalates* by Rosenheim (Ber. 1893, 26, 1191).

Tungsten forms ozosalts which are readily soluble and difficult to obtain free from the normal salts used in their preparation. The following have been described:—

Sodium ozotungsten oxalate

$$NaC_2O_4WO_4,5H_2O$$

and also the corresponding ammonium and calcium salts which have only 1 mol. of water of crystallisation (Mazzucchelli and Inghilleri, Atti. R. Accad. Lincei, 1908, [v.] 17, ii. 30).

Complex compounds of the tungstic acids with organic acids have been obtained by Grossmann and Krämer (Zeitsch. anorg. Chem. 1904, 41, 43); and by Mazzucchelli and Borghi (Gazz. chim. ital. 1910, 40, ii. 241); and additive compounds of the tetra-, penta-, and hexachloride with organic esters by Rosenheim and Loewenstamm (Ber. 1902, 35, 1115).

TURANITE *v.* VANADIUM.

TURANOSE. A sugar $C_{12}H_{22}O_{11}$ obtained by heating melezitose with acetic acid. Is not hydrolysed by any of the ordinary enzymes and is consumed very slowly by yeast. Rotatory power $[\alpha]_D = +71\cdot8$ shows no birotation (Tanret, Compt. rend. 1906, 1424) (*v.* CARBOHYDRATES).

TURF *v.* FUEL.

TURGITE *v. Iron oxides*, art. IRON.

TURKEY-RED OILS *v.* OILS, FIXED, and FATS.

TURMERIC (*Indian saffron; Terra merita*). The so-called turmeric root of commerce is the underground stem or rhizome of *Curcuma longa* (Linn.), or of various species of *Curcuma—e.g. C. tinctoria, C. viridiflora* (Roxb.), &c. These plants, belonging to the *Scitamineæ*, are indigenous to Southern Asia, and are there largely cultivated, being exported from China, Madras, Bengal, Java, Malabar, Batavia, and Barbados. Those varieties which are derived from the central rhizomes are more or less round (*Curcuma rotunda* [L.]), while the lateral rhizomes are long and finger-shaped (*C. longa*). When of good quality these commercial varieties are hard, and of a dull, waxy, resinous fracture, the external colour being yellowish-grey, and internally orange-brown, but producing, when ground, a somewhat bright yellow powder, having a strong characteristic odour and a peppery bitter taste.

The rhizome of *Canna speciosa*, a West African plant, is said to be exactly similar to East Indian turmeric in taste, smell, and chemical reactions (Daniell, Pharm. J. 19, 258). It is cultivated in Sierra Leone, and furnishes the so-called 'African turmeric.'

According to Pelletier and Vogel (Annalen, 44, 297), turmeric contains cellulose, gum, starch, mineral matter, a strong-smelling volatile oil, a brown colouring matter, and a characteristic yellow colouring matter named by them *Curcumin*. Pectin and pectic acid are also present (Schützenberger). Kachler (Ber. 3, 713) found a notable quantity of potassium binoxalate.

Pelletier and Vogel's method of isolating the curcumin consisted in first removing the fatty, resinous, and other impurities by extracting pulverised turmeric with water and carbon disulphide, then dissolving out the colouring matter with boiling alcohol, and purifying it by successive solution in ether and alcohol, precipitation with lead acetate, and subsequent treatment with hydrogen sulphide and extraction with ether. It was thus obtained as an amorphous yellow powder.

Lepage adopted a similar method, but after extraction with carbon disulphide the colouring matter was dissolved in alkali, precipitated with acid, and finally purified by means of ether.

Daube was the first to obtain curcumin in the crystalline state. He removed essential oil by passing a strong current of steam over the coarsely-ground turmeric, then thoroughly extracted it with hot water, and finally treated the dried residue with boiling benzene. On cooling the solution thus obtained, crude curcumin separated as bright orange-red crystalline crusts, which were pressed between blotting-paper, and dissolved in cold alcohol. After filtering off some yellow flocculent substance, the solution was precipitated with an alcoholic solution of neutral lead acetate, adding finally a little basic lead acetate in order to neutralise almost entirely the liberated acetic acid and prevent thereby any solution of the colour-lake. The brick-red precipitate was washed with alcohol, suspended in water, and decomposed with hydrogen sulphide. The liberated curcumin was extracted from the precipitate with boiling alcohol, from which it crystallised on slow evaporation.

Benzene is very suitable for obtaining pure curcumin, for although it is very little soluble in this liquid, the resinous impurities are not dissolved thereby.

Gajewsky (Ber. 3, 265) obtained crystalline curcumin by first extracting turmeric root with carbon disulphide, then dissolving out the colouring matter with ether, and purifying it by fractional crystallisation from ether or benzene. He detected the presence of another colouring matter and also traces of an alkaloid. This chemist obtained an increased yield of colouring matter by washing the dry ethereal extract with dilute ammonia to remove resin, then dissolving the brittle residue in boiling concentrated ammonia solution and precipitating with carbon dioxide; 250 grms. ethereal extract gave 100 grms. flocculent curcumin, m.p. 140°. Jackson (Ber. 14, 485) also obtained crystallised curcumin by first removing the oil by long extraction with carbon disulphide (60 hours), then thoroughly extracting (60 hours) with ether, and after washing the orange-coloured extract thus obtained with cold alcohol or ether, crystallising from hot alcohol.

Perkin (Chem. Soc. Trans. 1904, 85, 63) precipitates an alcoholic turmeric extract with lead acetate, washes the lead compound first with alcohol then with water, and decomposes it with dilute sulphuric acid. From the mixture of lead sulphate and curcumin, the latter is removed with boiling alcohol and the extract evaporated and poured into ether, which causes the separation of tarry impurities. The ethereal solution, after evaporation to a small bulk, is treated with carbon disulphide and allowed to stand, the crystals which separate from time to time being removed. 0·56 p.c. of curcumin was thus obtained from turmeric.

Curcumin crystallises from alcohol in orange-coloured prisms, m.p. 165° (Daube), 172° (Gajewsky), 178° (Jackson), and 183° (Ciamician and Silber, Ber. 30, 192), and is soluble in ether, forming a green fluorescent liquid. Alkaline solutions dissolve it with a reddish-brown colour, which when neutralised passes to yellow, and on this account it is useful in the form of 'turmeric paper' as a reagent for alkalis. Whereas Daube assigned to curcumin the formula $C_{10}H_{10}O_3$, Gajewsky $(C_4H_4O)_n$, probably $C_{16}H_{16}O_4$, Jackson considered that $C_{14}H_{14}O_4$ or $C_{28}H_{28}O_8$ were more reasonable expressions, and of these Jackson and Menke (Amer. Chem. J. 6, 78) preferred the former, and prepared the following derivatives harmonising with this view.

Dihydrocurcumin $C_{14}H_{16}O_4$, brownish-white powder, m.p. 100° *ca.*, *dihydrocurcumin anhydride* $C_{28}H_{30}O_7$, dirty white powder, m.p. 120° *ca.*, *diethylcurcumin* $C_{18}H_{22}O_4$, brownish tar, *p-brombenzyl curcumin* $C_{21}H_{19}BrO_4$, pale yellow crystals, m.p. 76°–78°, *acetylcurcumin* $C_{16}H_{16}O_5$, brownish mass, *diacetylcurcumin* $C_{18}H_{18}O_6$, yellow rhombic crystals, m.p. 154°, *curcumin-tetrabromide* $C_{14}H_{14}O_4Br_4$, powder, m.p. 185° *ca.*, *tetrabromcurcumin* $C_{14}H_{10}Br_4O_4$, red powder, *pentabromcurcumindibromide* $C_{14}H_9Br_5O_4 \cdot Br_2$, red powder, m.p. 120 *ca.*, *potassium curcumin* $KC_{14}H_{13}O_4$, red powder, and *dipotassium curcumin* $K_2C_{14}H_{12}O_4$, red needles. By fusion with alkali curcumin gives *protocatechnic acid*, when oxidised with permanganate *vanillin*, and the diethyl ether by similar treatment yields *vanillic acid ethyl ether*. Jackson and Menke represented curcumin by the following formula

$$C_6H_3(OH)(OCH_3)CH(C_5H_5)CO_2H$$
$$(CH{:}OCH_3 : OH = 1 : 3 : 4).$$

Ciamician and Silber (Ber. 30, 192), as the result of methoxy determinations, assigned the formula $C_{21}H_{20}O_6$ or $C_{19}H_{14}O_4(OCH_3)_2$ to curcumin, and prepared *diacetylcurcumin* $C_{21}H_{18}O_6(C_2H_3O)_2$, needles, m.p. 170°-171°; and *curcumin dimethyl ether* $C_{19}H_{12}O_2(OCH_3)_4$, yellow needles, m.p. 135°. Digested with hydroxylamine hydrochloride in alcoholic solution curcumin gave the compound

$$C_{21}H_{19}NO_5 (i.e.\ C_{21}H_{20}O_5NOH - H_2O),$$

needles, m.p. 178°, whereas phenylhydrazine gave a substance crystallising in colourless needles.

Perkin (Chem. Soc. Trans. 1903, 83, 140, and 1905, 85, 63) by means of alcoholic potassium acetate, obtained from curcumin the monopotassium salt $C_{21}H_{19}O_6K$, fine orange-red needles. A *benzoyl curcumin*, pale-yellow needles, m.p. 176°–178°, was also prepared and gave by the cryoscopic method numbers, harmonising with Ciamician and Silber's formula.

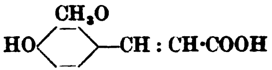
Molecular weight determinations, however, according to Jackson and Clarke (Ber. 1905, 38, 2712), indicated the correctness of the formula $C_{14}H_{14}O_4$, and again (*ibid.* 1906, 39, 2269) these authors pointed out that unless special care is employed Zeisel's method gives erroneous figures with curcumin. When heated with hydriodic acid at 120° a correct result is given, but above this temperature curcumin gives a colourless oil rich in iodine (75·75 p.c.), which reacts with the alcoholic silver nitrate solution.

Von Kostanecki and Lampe (*ibid.* 1910, 43, 2163) consider that Ciamician and Silber's formula $C_{21}H_{20}O_6$ correctly represents curcumin, and describe *dicarbomethoxy-curcumin*

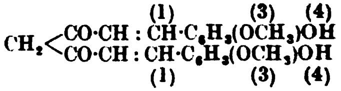
$$C_{19}H_{16}O_2(O{\cdot}COOCH_3)_2(OCH_3)_2,$$

yellow prisms, m.p. 150°, and *dicarbethoxy curcumin*, yellow leaflets, m.p. 149°–150°.

When curcumin is boiled with potassium hydroxide solution, *vanillic acid* and *ferulic acid*

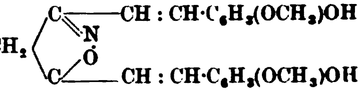


are produced. As a result these authors consider that the constitution of this colouring matter is as follows—



$$CH_2 \begin{cases} \overset{(1)}{CO{\cdot}CH : CH{\cdot}C_6H_3}(\overset{(3)}{OCH_3})\overset{(4)}{OH} \\ \underset{(1)}{CO{\cdot}CH : CH{\cdot}C_6H_3}(\underset{(3)}{OCH_3})\underset{(4)}{OH} \end{cases}$$

Further support for this formula is given by the fact that curcumin, like β-diketones, gives when treated with hydroxylamine an *iso*-oxazole derivative, and the compound prepared by Ciamician and Silber is probably *4·4′-dihydroxy-3·3′-dimethoxy-a : γ-distyrylisoxazole*



It is well known that a mixture of boric and hydrochloric acids imparts to turmeric paper a brown colour which is turned blue by alkalis. This reaction was investigated by Schlumberger (Bull. Soc. Chem. [ii.] 5, 194), who found that when an alcoholic extract of turmeric is heated in a sealed tube with boric acid, a red crystalline boric acid derivative is produced, soluble in alkaline solutions with a purple-violet colour. Boiling water decomposes this compound with elimination of boric acid, and formation of *pseudo-curcumin*, a yellow powder. If the alcoholic solution of the boric acid compound is digested with strong hydrochloric acid, a black substance separates, whereas boric acid remains in the liquid. On extracting the black powder with a mixture of alcohol and acetic acid, the filtrate deposits green iridescent crystals of rosocyanine.

Rosocyanine is readily soluble in alcohol containing a trace of mineral acid and dissolves in ammonia solution with a blue colour. It is according to Schlumberger, an unstable substance, and if boiled for a long time with alcohol, is converted into pseudo-curcumin.

Jackson and Clarke (*l.c.*) prepared rosocyanine by heating a solution of curcumin in dilute alcohol with boric and sulphuric acids, and describe it as a purplish-red powder, closely resembling powdered rosaniline. These authors consider it to be isomeric with curcumin $C_{14}H_{14}O_4$, and describe an *ammonium salt* $C_{14}H_{13}O_4NH_4$, and a *potassium salt* $C_{14}H_{13}O_4K$, both of which possess an intense blue colour. The tinctorial properties of curcumin are of special interest, for not only is it a strong colouring matter towards mordants, but with cotton, wool and silk behaves also as a substantive dyestuff. In the latter case it is only necessary to add the material to a boiling decoction of the colouring matter. Though considerably employed up to within recent years by the wool and silk dyer in the formation of olives, browns, and other compound colours turmeric is now but rarely employed for dyeing purposes in England. In India, however, it appears to be still in vogue.

Cotton is usually dyed in a decoction of turmeric rendered slightly acid by the addition of a little acetic acid, or alum may be employed. The colour does not resist either the action of light or of alkalis, and readily acquires a brownish-red tint. Wool may be dyed without any addition, keeping the temperature about 60°. By previously mordanting with alum a brighter effect is produced, whereas tin mordant gives a more orange colour. Potassium dichromate and ferrous sulphate employed in a similar manner yield respectively olive and brown coloured shades.

Silk is preferably dyed in an acid bath, and is sometimes previously mordanted.

Turmeric oil is the thick orange-coloured aromatic oil present to the extent of 3·23 p.c. in turmeric from which it can be extracted by means of carbon disulphide. Bolley examined the portion distilling over at 230°–250°, and considered it to be identical with carvol, whereas Gajewsky (*l.c.*) found the portion distilling over at 220°–228° contains less carbon and more hydrogen than that which passes over at a higher temperature. On oxidising the latter portion with chromic acid, an acid oil is obtained which contains valeric, caproic, and terephthalic acids. Jackson and Menke (*l.c.*) analysed that portion which distils over at 285°–290°, and gave it the formula $C_{19}H_{28}O$, and the name *turmerol*, and obtained *turmeryl chloride* $C_{19}H_{27}Cl$, *sodium turmerol* $C_{19}H_{27}ONa$, and *turmerol* iso*butyl ether* $C_{19}H_{27}O{\cdot}C_4H_9$. With permanganate turmerol gave *terephthalic acid*, *turmeric acid* $C_{11}H_{14}O_2$, and *apoturmeric acid* $C_{10}H_{12}O_4$ or $C_{10}H_{10}O_4$. According to Rupe (Ber. 1907, 40, 4909) when turmeric oil is boiled with dilute sodium hydroxide solution a substance, b.p. 156°/12 mm., apparently not identical with Jackson and Menke's turmerol, is produced. Stronger alkali yields an optically active ketone $C_{13}H_{18}O$, *curcumone*, b.p. 119°–120°/8 mm., which gives a semicarbazone, m.p. 119·5°–120·5°, an oxime, b.p. 159°/11 mm., and condensation products with aromatic aldehydes. With permanganate the ketone gives p-*methylacetophenone* and *terephthalic acid*, and with alkaline hypobromite the acids $C_{12}H_{16}O_3$, m.p. 150°, and $C_{12}H_{16}O_2$, m.p. 33°–34°. By the further action of permanganate the latter yields a dicarboxylic acid $C_{12}H_{14}O_4$, m.p. 228°. Rupe) Luksch, and Steinbach (Ner. 1909, 42, 1515, were unable to isolate from turmeric oil the turmerol of Jackson and Menke having sp.gr. 0·9388 at 20° and $[\alpha]_D^{20}$ −27·46. By digestion with alcohol and 30 p.c. potassium hydroxide solution the ketone $C_{13}H_{18}O$, *curcumone* was obtained, which has b.p. 121°/10 mm., sp.gr. 0·9566 at 20°, n_D 1·50526, $[\alpha]_D$ 80·55, and yields the p-*bromophenylhydrazone*, m.p. 71°. It condenses with benzaldehyde to form the compound $C_{13}H_{16}O : CH{\cdot}C_6H_5$, m.p. 106°, and with piperonal and anisic aldehyde similar compounds melting respectively at 86° and 77°–78° are produced.

The acid $C_{12}H_{16}O_2$ (*l.c.*), m.p. 33°–34°, is called *curcumic acid*, and appears to be identical with Jackson and Menke's turmeric acid (Rupe and Steinbach, Ber. 1910, 43, 3465). By oxidation with permanganate it gives terephthalic acid, *p*-tolymethylketone, and the acid $C_{12}H_{14}O_4$, m.p. 226°–228° (*l.c.*), and this possibly consists of apoturmeric acid (J. and M.). Although it was considered that curcumic acid might be *γ*-*p*-tolylvaleric acid, the synthesis of this latter compound showed that the two substances are not identical but similar (*ibid.* 1911, 44, 584). Again curcumic acid is not *p*-tolyl-*α*-methylbutyric acid (Rupe and Bürgin, *ibid.* 1218). Rupe and Steinbach (*l.c.*) consider that curcumone is to be regarded as a benzene derivative containing two parasubstituents, one being methyl, and the second, one or other of the groups $\cdot CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$,

$\cdot CHMe{\cdot}CHMe{\cdot}COMe$, or $.CMeEt{\cdot}COMe$,

whereas in curcumic acid the group COMe is replaced by COOH. *See* also Schimmel & Co. (Bericht, April, 1911). A. G. P.

TURMERIC ACID *v.* Turmeric.

TURMERINE *v.* Primuline and its derivatives.

TURMERYL CHLORIDE *v.* Turmeric.

TURNBULL'S BLUE. A variety of Prussian blue, *v.* Cyanides.

TURNER'S YELLOW. *Patent yellow.* Lead oxychloride $3PbO{\cdot}PbCl_2$.

TURNIP. A biennial, cruciferous plant, producing in the first year a large root stock containing a store of carbonaceous and nitrogenous matter intended for the formation of flower-stem and seeds in the second year. This 'root' is the chief valuable product for which the crop is grown. Many varieties, differing in the shape, size, and colour of the root, are known, but they may all be classed as belonging to two species—the 'white turnip,' or simply 'turnip' *Brassica rapa* (Linn.), or *B. rapa rapifera* (Metzger), and the 'Swedish turnip,' or 'Swede,' known often as 'ruta-baga' in America, *Brassica campestris rutabaga* (Linn.), or *B. napus esculenta* (DC.). There are many varieties of each, but as a rule 'turnips' have rougher leaves, of greener colour, and the root has white, or, in some cases, yellow flesh; whilst 'swedes' possess smoother leaves of a bluish-green colour, and the roots have yellow flesh. The leaves of the turnip spring directly from the root, whilst those of the swede arise from a distinctly marked 'neck.'

Both types grow best in cool, damp climates; in hot, dry countries the roots tend to become very woody and fibrous. Swedish turnips resist frost better, and can be grown in stiffer soils than the white varieties; they also keep better after gathering.

According to König, the following figures represent the average composition of the two types—

	Water	Protein	Fat	Sugar	Other N-free ext.	Fibre	Ash
White turnips	90·67	1·12	0·24	2·55	3·55	1·11	0·76
Swedes .	88·88	1·39	0·18	3·02	4·35	1·44	0·74

Great variations in composition, however, have been observed, the most important factors, in order of importance, being apparently, season, variety, size of root, district, and soil. Even with the same variety, grown under the same conditions, and with roots of approximately the same size, considerable variations in the composition of individual roots are found, especially in the amount of sugar. Thus, Collins (J. Soc. Chem. Ind. 1901, 20, 536) found in 25 individual roots of XL All swedes, the proportion of sugar varied from 4·5 to 7·8 p.c., with an average of 6·27 p.c.

The variation with season is considerable; Collins, as the average of 12 varieties of swedes grown in 1900, found a sugar content of 6·26 p.c., while the same varieties, in 1901, gave an average of only 4·05 p.c. of sugar. Analogous to the effect of season is that of local climate; even in Britain this effect is seen. In 1904 several varieties of swedes were grown simultaneously in Cambridgeshire, Norfolk (2 centres), and Ross-shire (4 centres), and the resulting crops were examined for dry matter and sugar content.

The following figures show the sugar contents of 5 varieties, as grown at the various centres—

Variety	Cambridge	Norfolk 1	Norfolk 2	Norfolk Mean	Ross-shire 1	Ross-shire 2	Ross-shire 3	Ross-shire 4	Ross-shire Mean
Fell's Bronzetop	6·5	6·1	8·0	7·0	7·2	7·3	7·1	8·0	7·4
New Arctic .	6·1	6·0	8·1	7·0	6·9	7·2	7·1	7·9	7·3
Magnum Bonum	6·3	5·7	7·6	6·6	6·8	7·2	6·6	8·1	7·2
XL All . .	6·0	6·0	7·4	6·7	6·8	6·8	6·7	7·5	7·0
Carter's Elephant	6·3	5·6	7·0	6·3	6·7	6·9	6·8	7·4	7·0
Average . .	6·2	5·9	7·6	6·7	6·9	7·1	6·9	7·8	7·2

These results clearly show that the roots grown in the moist, cool climate of Ross-shire were, on the average, richest in sugar, while those grown in the hot, dry climate of Cambridgeshire were the poorest (Guide to Expts. 1906, Dept. of Agric. Univ. of Cambridge).

So, too, Hendrick (Bull. 1, Coll. Agric. Univ. of Aberdeen, 1904) found, as the average of analyses of 21 varieties of swedes, grown in Aberdeenshire, 11·7 p.c. of dry matter, and 5·15 p.c. of sugar, while 9 varieties of turnips yielded an average of 9·48 p.c. of dry matter, and 4·55 p.c. of sugar; and Wood (Guide to Expts. Dept. of Agric. Univ. of Camb. 1906) found as the mean of the analyses of 5 varieties of swedes, grown in Cambridgeshire (1 centre) and Norfolk (2 centres), 10·8 p.c. of dry matter and 6·6 p.c. of sugar, and for 7 varieties of white turnips 7·81 p.c. of total dry matter, and 4·24 p.c. of sugar.

The effect of soil upon the composition of the roots, although perceptible, is not great. That of manuring is very great upon the yield, but is comparatively small upon the composition, except in so far as it affects the size of the roots.

The effect of size of root, in any variety, is considerable, small roots being invariably richer in solid matter, especially sugar, than large ones. This is well seen from the following analyses by Hendrick (J. Soc. Chem. Ind. 1897, 16, 213) of two samples of 'Achilles' turnips—

Average wt. of 1 root	Water	Dry matter	Sugar	Total N	Alb. N	Ash
5lb. 1oz.	92·8	7·2	3·93	0·192	0·108	0·56
2lb. 14oz.	91·3	8·7	4·62	0·148	0·076	0·64

In view of these many circumstances affecting the composition of the roots, it is obviously of little value to attempt to give any representative composition of turnips.

It may, however, be of interest to quote the figures given by Kellner and by Warington as representing the average composition of turnips and swedes.

Kellner gives—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Swedes	87·8	1·5	0·2	8·2	1·3	0·9
Turnips	91·5	0·9	0·1	6·0	0·8	0·7

Warington's figures are—

	Water	Proteids	Amides, etc.	Fat	N-free extract	Crude fibre	Ash
Swedes	89·3	0·7	0·7	0·2	7·2	1·1	0·8
Turnips	91·5	0·5	0·5	0·2	5·7	0·9	0·7

The protein, *i.e.* total N×6·25, in the above analyses, contains a considerable and variable quantity of non-proteid substance. König states that from 35 to 55 p.c. of the total nitrogen is present, partly as amides or amino acids, partly as nitrates. Warington estimates the non-albuminoid nitrogen in turnips at 49 p.c. of the total nitrogen, but gives as the average *digestible* albuminoids 0·2 p.c. in swedes, and 0·1 p.c. in turnips. Collins (*l.c.*) found, in 'Monarch' swedes, the real albuminoids varied from 0·47 to 0·63 p.c., while the amides, &c., ranged from 0·34 to 0·61 p.c. Hendrick (*l.c.*) found the proportion of non-albuminoid nitrogen to total nitrogen varied from 27 to 42 p.c. in yellow turnips, and from 23 to 59 p.c. in 'Best of All' swedes. In the days when the 'nitrogenous substances' or 'albuminoids' in foodstuffs, were estimated by multiplying the total nitrogen by 6·25, turnips, in common with other roots, gave results on analysis which indicated that they possessed greater feeding value than actual experience showed them to have. If, however, distinction is made between true proteids and amino compounds, amides, and nitrates, the nutritive value of turnips, as assessed by analysis, seems, in most cases, to be much less than their actual efficiency as foods (*v.* Ingle, Trans. High. & Agric. Soc. Scotland. 1910, 22, 178; also Hendrick, *ibid.* 150). It would seem, in fact, that either the true albuminoids in turnips are much more digestible than has hitherto been admitted, or, more probably, that the amino compounds may, under certain conditions, behave like albuminoids, in building up animal tissue.

The sugars present in turnips are dextrose, lævulose, and sucrose, the invert sugars largely predominating. The other N-free extractives include pectins, pentosans, and cellulose.

The ash of turnips varies greatly in composition and amount. According to figures compiled by König, the whole ash varies from 4·9 to 14·0 p.c. of the dry matter, while the potash in the ash may range from 26 to 62 p.c., the lime from 5·5 to 15·9 p.c., and the phosphorus pentoxide from 5·5 to 18·9 p.c. The mean of 32 analyses of the ash gave—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
45·4	9·8	10 6	3·7	0·8	12·7	11·2	1·9	5·0

The upper half of a root is richer in solid matter than the lower, and due allowance must be made for this fact in sampling turnips for analysis.

Turnip leaves are sometimes used for feeding purposes; according to Kellner they contain, on the average—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
88·4	2·2	0·5	5·3	1·5	2·1

Turnips, like other plants of the genus *Brassica*, contain thio compounds, and when they decay or even suffer slight decomposition by boiling, they evolve unpleasant-smelling sulphur compounds, among which mercaptans are probably included.

Turnips require liberal supplies of phosphates, and phosphatic manures, generally superphosphates, are almost invariably used for this crop. For a study of the destination of phosphates and nitrogen when applied as a manure to turnips, *v.* Somerville and Smith (J. Soc. Chem. Ind. 1897, 16, 19). H. I.

TURPENTINE *v.* OILS, ESSENTIAL; also TERPENES.

TURPENTINE VARNISH *v.* VARNISH.

TURPETH or **TURBITH MINERAL.** An old name for basic mercuric sulphate $HgSO_4{\cdot}2HgO$, sometimes called Queen's yellow, *v.* MERCURY.

TURPETH or **TURBITH ROOT.** The root of the convolvulaceous plant *Ipomœa Turpethum* (R.Br.) [*Operculina Turpethum* (Peter)], found in India and Australia. It contains a volatile oil and a drastic resin, *turpethin* $C_{34}H_{56}O_{16}$, isomeric with jalapin and scammonin. When treated with dilute mineral acids this substance is hydrolysed into glucose and *turpetholic acid* $C_{16}H_{32}O_4$ (*v.* Boutron-Charlard, J. Pharm. Chim. 8, 131; Spirgratis, J. pr. Chem. [I.] 92, 97).

TURPETHIN *v.* GLUCOSIDES.

TURQUOISE or **CALAITE** (*Türkis*, Ger.). A gem-stone which has often been regarded as a hydrated aluminium phosphate

$$2Al_2O_3{\cdot}P_2O_5,5H_2O,$$

accidentally coloured by copper and iron phosphates. It has been shown, however, by S. L. Penfield (Amer. J. Sci. 1900, 10, 346) that the latter enter into the constitution of the mineral, and he writes the formula as—

$$[Al(OH)_2,Fe(OH)_2,Cu(OH),H]_3PO_4$$

representing a derivative of orthophosphoric acid with the hydrogen atoms largely replaced by the univalent radicles $Al(OH)_2$, &c. In some analyses approximately two-thirds of the hydrogen atoms are so replaced, and the formula becomes $R_2'HPO_4$. The amount of copper ranges from 2·0 to 8·5 p.c. CuO, and the iron from 0·1 to 4·0 p.c. Fe_2O_3. The mineral is soluble in hydrochloric acid without discoloration; when heated it loses water and blackens. It is opaque (or translucent in thin chips) with a sky-blue to green colour, and on the polished surface shows a soft, waxy lustre; sp.gr. 2·6–2·8; H. 6. Turquoise occurs as cryptocrystalline masses, sometimes with nodular or stalactitic surfaces, in crevices in rocks, more especially in those of volcanic origin. The best quality of material has for centuries been mined near Nishapur in Persia, and being exported to the west through Turkey it came to be known as turquoise. Deposits in the Sinai Peninsula were worked by the ancient Egyptians. Ancient mines, worked in prehistoric times, are also known in Mexico and in the state of New Mexico. Considerable quantities (17 tons in 1909, and 8¼ tons in 1910) are now obtained from Nevada, New Mexico, Arizona, California, and Colorado (D. B. Sterrett, Min. Res. U.S., Annual Reports for 1910 and earlier). Recently, minute crystals of turquoise have been described from Campbell Co., Virginia; these are triclinic and isomorphous with chalcosiderite (W. T. Schaller, Amer. J. Sci. 1912, 33, 35).

Turquoise has been imitated by subjecting to pressure a mixture of aluminium and copper phosphates. Very clever imitations are also made of glass; these may be detected by the bright, glassy, conchoidal fracture when chipped at the edges—the fracture of turquoise being dull and finely granular.

Bone-turquoise or *odontolite* is fossil bone or ivory coloured by the iron phosphate vivianite, or perhaps sometimes artificially stained by a copper solution. It can be recognised under the microscope by its organic structure. It effervesces with acid, and gives a smell of burning when heated. L. J. S.

TUTENAG or **TUTENAGUE.** *Chinese silver. Packfong.* An alloy resembling German silver.

TYPE METAL *v.* TIN.

TYRIAN PURPLE *v.* PURPLE OF THE ANCIENTS.

TYROSINE, p-*hydroxyphenylalanine*, p-*hydroxy-β-phenyl-α-aminopropionic acid*

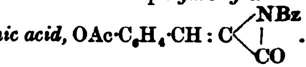
$$HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2)CO_2H,$$

was so named by Liebig, who first obtained it by fusing freshly prepared cheese (τυρός) with caustic potash (Annalen, 1846, 57, 127). It occurs widely spread both in the animal and vegetable kingdoms, forming one of the most common products of proteid hydrolysis, and occurring in the free state in the seedlings and young shoots of the vetch (*Vicia sativa*) (Gorup-Besanez, Ber. 1877, 10, 781), the gourd (*Cucurbita pepo*) (Schulze and Barbieri, *ibid.* 1878, 11, 710, 1233); the lupins (*Lupinus luteus*, *L. albus*) (Schulze, *ibid.* 1878, 12, 1924; Wassilieff, Landw. Versuchs Stat. 1901, 55, 45); in the tubers of potatoes (*Solanum tuberosum*) (Schulze, Ber. 1879, 12, 1924), the swede (*Brassica rapa*), the dahlia (*Dahlia variabilis*) (Borodin, Botan. Zeit. 1882, 590; Leitgeb, Chem. Zentr. 1888, 1397; Bertrand, Compt. rend. 1896, 122, 1215); in the tubercules of *Stachys tubifera* (Planta and Schulze, Ber. 1890, 23. 1698); in the juice of sugar beet (*Beta vulgaris*) (v. Lippmann, *ibid.* 1884, 17, 2835), in celery (*Apium graveolens*) (Bamberger and Landsiedl, Monatsh. 1904, 25, 1030); in the unripe seeds of the French bean (*Phaseolus vulgaris*) (Pfenninger, Ber. Deut. bot. Ges. 1909, 27, 227), the pea (*Pisum sativum*) (Schulze and Winterstein, Zeitsch. physiol. Chem. 1910, 65, 431); in the green pods of the broad bean (Bourquelot and Hérissey (J. Pharm. Chim. 1898 [vi.] 8, 385); in the juice of elderberries (*Sambucus nigra*) (Sack and Tollens, Ber. 1904, 37, 4115); in fungi (Winterstein, Zeitsch. physiol. Chem. 1899, 26, 438). In the animal kingdom, tyrosine is found in caterpillars, crabs, spiders, and beetles (v. Lippmann, *l.c.*) and in cochineal (Warren de la Rue, Annalen, 1848, 64, 1); in the larva of *Lucilia Caesar* (Gossard, Compt. rend. 1904, 139, 644); it occurs in Emmenthaler and in Roquefort cheeses (Benecke and Schulze, Landw. Jahrbücher, 1887, 16, 317; Winterstein and Thöny, Zeitsch. physiol. Chem. 1902, 36, 28; Dox, J. Amer. Chem. Soc. 1911, 33, 423). Under normal conditions, tyrosine is not found in the liver or blood of men and animals, but occurs under certain pathological conditions (Frerichs and Staedeler, J. 1856, 702; Hoppe-Seyler, Zeitsch. physiol. Chem. 1881, 5, 348; Neuberg and Richter, Deut. med. Wochensch. 30, 499; Huber, Archiv. Heilkunde, 18, 485; Wyss, Schweiz. Zeitsch. Heilkunde, 1864).

Preparation. Tyrosine is most conveniently prepared from silk by hydrolysing with fuming hydrochloric acid, and evaporating the product under reduced pressure to dryness; the residue is dissolved in water and a stream of ammonia passed through the solution; it is then again evaporated to dryness, and the residue treated with cold water, when the tyrosine is left undissolved; or the whole residue may be boiled with water and animal charcoal, and from the filtrate pure tyrosine crystallises out quantitatively: one kilo of silk yielding 50·65 grms. of tyrosine (Abderhalden, Zeitsch. physiol. Chem. 1912, 77, 75; Abderhalden and Teruuchi, *ibid.* 1906, 48, 528).

Synthesis. Staedeler (Annalen, 1860, 116, 57) was the first to show that tyrosine was an aromatic compound, since it yielded chloranil (tetrachloroquinone) on treatment with chlorine; but its constitution as *p*-hydroxy-*β*-phenyl-*a*-aminopropionic acid was not established until 1882 when Erlenmeyer and Lipp (Ber. 1882, 15, 1544; Annalen, 1883, 219, 161) prepared racemic tyrosine from phenylacetaldehyde by the following series of reactions: *phenylacetaldehyde* on treatment with hydrogen cyanide gave *phenyllactonitrile*; this was converted by ammonia into the *nitrile of phenylalanine* which, on hydrolysis, gave *phenylalanine*; p-*nitrophenylalanine* on reduction gave the corresponding amino compound from which p-*hydroxyphenylalanine* (*r*-tyrosine) was produced by the action of nitrous acid.

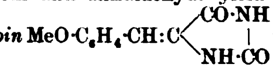
$$\begin{aligned}\mathrm{C_6H_5{\cdot}CH_2{\cdot}CHO} &\rightarrow \mathrm{C_6H_5{\cdot}CH_2{\cdot}CH(OH)CN}\\ &\rightarrow \mathrm{C_6H_5{\cdot}CH_2{\cdot}CH(NH_2)CN}\\ &\rightarrow \mathrm{C_6H_5{\cdot}CH_2{\cdot}CH(NH_2)CO_2H}\\ &\rightarrow \mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2)CO_2H}\\ &\rightarrow \mathrm{NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2)CO_2H}\\ &\rightarrow \mathrm{HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2)CO_2H}\end{aligned}$$

A more convenient method of synthesis is that due to Erlenmeyer jun., and Halsey (Annalen, 1899, 307, 138), in which *p*-hydroxybenzaldehyde and hippuric acid condense in the presence of acetic anhydride and anhydrous sodium acetate to form the *acetyl derivative* of the *lactimide* of p-*hydroxy-a-benzoylaminocinnamic acid*,  $\mathrm{OAc{\cdot}C_6H_4{\cdot}CH:C}\left\langle\begin{array}{l}\mathrm{NBz}\\ \,|\\ \mathrm{CO}\end{array}\right.$. This, on hydrolysis with alkali, gives p-*hydroxy-a-benzoylaminocinnamic acid*

$$\mathrm{HO{\cdot}C_6H_4{\cdot}CH:C(NHBz)CO_2H}$$

from which by reduction *benzoyltyrosine*

$$\mathrm{HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NHBz)CO_2H}$$

is obtained and converted by hydrolysis with acids into r-*tyrosine.* Another method of synthesis which can also be extended to the preparation of halogenated derivatives of tyrosine is described by Wheeler and Hoffmann (Amer. Chem. J. 1911, 45, 368; *cf.* Wheeler, Hoffmann and Johnson, Bio-Chem. J. 1911, 10, 147; Johnson and Bengis, J. Amer. Chem. Soc. 1912, 34, 1061). This method consists in condensing a suitable aldehyde with hydantoin, reducing and hydrolysing the product; thus hydantoin and anisaldehyde yield *anisylidenehydantoin*  $\mathrm{MeO{\cdot}C_6H_4{\cdot}CH:C}\left\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \qquad\ \ |\\ \mathrm{NH{\cdot}CO}\end{array}\right.$ which, when boiled with hydrogen iodide is converted into *tyrosine* together with a small quantity of 4-p-*hydroxybenzoylhydantoin* (*tyrosinehydantoin*)

$$\mathrm{OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH}\left\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \\ \mathrm{NH{\cdot}CO}\end{array}\right.$$

from which tyrosine can be obtained by boiling with baryta water.

Properties. *l*-Tyrosine, the natural product, is also obtained by the resolution of *d*-*al*-benzoyltyrosine through its brucine salt and subsequent hydrolysis of the *l*-benzoyltyrosine. It crystallises in long flexible silky needles, soluble in 2491 parts of water at 17° (Erlenmeyer and Lipp, *l.c.*), more readily soluble in hot water; dissolves in 13,500 parts of cold 90 p.c. alcohol (Staedeler, *l.c.*), insoluble in acetone, ether or absolute alcohol. It melts and decomposes at 314°–318° (corr.) when rapidly heated (Fischer, Ber. 1899, 32, 3638); at 295° (Cohn, Zeitsch. physiol. Chem. 1896, 22, 166); at 272° (Habermann and Ehrenfeld. *ibid.* 1902, 37, 18); 287° (Trans. Guinness Lab. 1903, i. 57). *l*-Tyrosine is lævorotatory both in acid and in alkali solution; the specific rotation varies with the concentration. For a 4 p.c. solution in 21 p.c. hydrochloric acid, the natural product has $[a]_D^{16}=-7{\cdot}98°$ (Mauthner, Monatsh. 1882, 3, 345), $[a]_D^{20}=-8{\cdot}07°$ (Landolt, Ber. 1884, 17, 2838); $[a]_D=-8{\cdot}48°$ (Schulze, Zeitsch. physiol. Chem. 1884, 9, 98); the synthetic product has $[a]_D^{20}=-8{\cdot}64°$ (Fischer, Ber. 1899, 32, 3638). In a 4·6 p.c. solution in 4 p.c. hydrochloric acid, the synthetic compound has $[a]_D^{20}=-13{\cdot}2°$ (Fischer), and the natural product $[a]_D^{16}=-14{\cdot}6°$ to $-16{\cdot}1°$ (Schulze and Winterstein, Zeitsch. physiol. Chem. 1902, 35, 299); in a 5·8 p.c. solution of 11·6 p.c. potassium hydroxide, the natural product has $[a]_D-9{\cdot}01°$ (Mauthner, *l.c.*). The molecular heat of combustion is 1071·2 Cal., heat of formation 156·4 Cal. (Berthelot and André, Compt. rend. 1890, 110, 884). The affinity constants of tyrosine are: first acid dissociation constant $K_a=4\times10^{-9}$, second acid dissociation constant $Ks=4\times10^{-10}$, basic dissociation constant $Kb=2{\cdot}6\times10^{-12}$ (Kanitz, Pflügers Archiv. 1907, 118, 539). The single band ultra violet absorption spectrum exhibited by solutions of tyrosine, is practically identical with that of proteids containing tyrosine; gelatin, and other proteids that contain no tyrosine show continuous spectra (Blyth, Chem. Soc. Trans. 1899, 1164).

d-Tyrosine, obtained by the resolution of *dl*-benzoyltyrosine through its cinchonine salt and subsequent hydrolysis, has $[\alpha]_D^{20}+8{\cdot}64°$ in 4·6 p.c. solution of 21 p.c. hydrochloric acid (Fischer); the dextrorotatory tyrosine obtained by v. Lippmann from the white shoots of sugar beet gave $[\alpha]_D+6{\cdot}85°$ in 25 p.c. hydrochloric acid; a feebly dextrorotatory tyrosine was found by Winterstein and Thöny (Zeitsch. physiol. Chem. 1902 36, 28) in a very old Emmenthaler cheese.

dl-Tyrosine prepared by hydrolysis of the synthetic benzoyl derivative crystallises in stout needles, melting and decomposing at 316° (corr.) when rapidly heated (Fischer, *l.c.*); its hydrochloride is much less soluble in concentrated hydrochloric acid than are the salts of the optically active forms, and the racemic compound can thus be separated from admixture with *d*- and *l*-tyrosine. By fermentation with large amounts of yeast in the presence of sugar and nutritive salts, tyrosine is converted to the extent of 60–80 p.c. into p-*hydroxyphenylethanol* (*tyrosol*) $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2OH$, m.p. 93°, b.p. 310°. The *dibenzoyl derivative* melts at 111°; tyrosol is also obtained by the action of yeast on *p*-hydroxyphenylethylamine (Ehrlich, Ber. 1911, 44, 139; Ehrlich and Pishtschimuka, *ibid.* 1912, 45, 1006).

By putrefactive decomposition, tyrosine is successively broken down into hydro-*p*-coumaric acid $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, *p*-hydroxyphenylacetic acid $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$, *p*-cresol and phenol (Baumann, Ber. 1880, 13, 279; Zeitsch. physiol. Chem. 1880, 4, 304). The administration of tyrosine to normal animals causes the production of phenol in the urine, but no excess of hydroxy acids (Blendermann, *ibid.* 1882, 6, 234; Bied. Zentr. 1883, 209; Cohn, Zeitsch. physiol. Chem. 1894, 14, 189), except in one case when a man took 50 grms. of tyrosine in 24 hours, and this produced alcaptonuria, homogentisic acid being found in the urine (Abderhalden, *ibid.* 1912, 77, 454). Inactive tyrosine administered to cats undergoes selective decomposition, so that the urine contains more of the dextro- than of the naturally occurring lævo- variety, and on evaporating the neutral or alkaline urine containing the tyrosine, it is converted into the corresponding uramino acid which, on subsequent treatment with acid, readily loses water, yielding tyrosine hydantoin (Dakin, J. Biol. Chem. 1910, 8, 25). In the case of alcaptonurics, the administration of tyrosine or certain derivatives of tyrosine, such as mono-palmyl-*l*-tyrosine, distearyl-*l*-tyrosine, *p*-aminotyrosine, causes an increase in the amount of homogentisic acid excreted (Abderhalden and Massini, Zeitsch. physiol. Chem. 1910, 66, 140; Wolkow and Baumann, *ibid.* 1891, 15, 228).

Detection and estimation. Tyrosine develops a red colour when warmed with Millon's reagent. When tyrosine is dissolved in a few drops of warm concentrated sulphuric acid, and the diluted solution neutralised with barium carbonate the filtrate gives a beautiful violet colour with ferric chloride (Pirea, Annalen, 1852, 82, 252). If a few drops of a solution of tyrosine are added to 2 c.c. of sulphuric acid containing 3 to 5 drops of a solution of aldehyde in twice its volume of alcohol of 90°, the liquid acquires a gooseberry red colour, the intensity of which is proportionate, between certain limits, to the quantity of tyrosine present (Denigés, Compt. rend. 1900, 130, 583). When tyrosine is added to a reagent consisting of 1 part of formalin, 45 parts of water and 55 parts of concentrated sulphuric acid, a green coloration is developed on boiling the mixture (Mörner, Zeitsch. physiol. Chem. 1902, 37, 86).

Tyrosine develops a rose-red colour under the influence of *tyrosinase*, the colour changing to a dirty violet, and finally a black precipitate of *melanin* is deposited (*v. Tyrosinase*, art. FERMENTATION).

Tyrosine is readily estimated by titration with N/5 sodium bromate in the presence of hydrochloric acid and sodium bromide, the liberated bromine being absorbed by the tyrosine with formation of dibromotyrosine (Millar, Trans. Guinness Lab. 1903, I. Part 1; Brown and Millar, Chem. Soc. Trans. 1906, 145).

Salts and derivatives. *l*-Tyrosine forms crystalline salts with mineral acids which dissociate in water, the *hydrochloride* $C_9H_{11}O_3N{\cdot}HCl,2H_2O$, *hydrobromide* $C_9H_{11}O_3N{\cdot}HBr$, *hydriodide*

$C_9H_{11}O_3N.HI$,

nitrate $C_9H_{11}O_3N{\cdot}HNO_3$ and *sulphate*

$C_9H_{11}O_3N{\cdot}H_2SO_4$

are described (Haushofer, J. 1883, 1177; Aloy and Rabaut, Bull. Soc. chim. 1908, [iv.] 3, 391; Staedeler, Annalen, 1860, 116, 64); the *platinichloride* $(C_9H_{11}O_3N{\cdot}HCl)_2PtCl_4$ forms yellowish-brown readily soluble crystals (Gintl, Zeitsch. Chem. 1869, 704); the *picrolonate* blackens and sinters at 260° (Levene and van Slyke, J. Biol. Chem. 1912, 12, 127). The following metallic salts have been prepared, those of the heavy metals and the alkaline earth metals are sparingly soluble: the *copper salt* $(C_9H_{10}O_3N)_2Cu$ dissolves in 1230 parts of cold or 240 parts of boiling water (Hofmeister, Annalen, 1877, 189, 24); the *silver salts* $C_9H_9O_3NAg_2,H_2O$,

$C_9H_{10}O_3NAg,\frac{1}{2}H_2O$ and $C_9H_{10}O_3NAg$;

the *mercury salts*, $C_9H_{11}O_3N{\cdot}2HgO,2H_2O$, $C_9H_{11}O_3N{\cdot}2HgO,H_2O$ and $C_9H_{11}O_3N,3HgO,H_2O$, the *barium salt* $(C_9H_{10}O_3N)_2Ba$; *calcium salt* $C_9H_9O_3NCa$, the *mercury-calcium salt*

$(C_9H_9O_3N)_2CaHg$,

and the *sodium salt* $C_9H_9O_3NNa_2$ (Vintschgau, J. 1869, 985; Baumann, Zeitsch. physiol. Chem. 1880, 4, 320; Causse, Compt. rend. 1900, 130, 1196).

l-*Tyrosine methyl ester* $C_9H_{10}O_3N{\cdot}CH_3$ forms colourless prisms, m.p. 135°–136° (corr.); $[\alpha]_D^{20}+25{\cdot}75°$ in methyl alcohol solution; the *hydrochloride* $C_9H_{10}O_3N{\cdot}CH_3,HCl$ forms colourless needles; l-*tyrosine ethyl ester*

$C_9H_{10}O_3N{\cdot}C_2H_5$,

has m.p. 108°–109°, $[\alpha]_D^{20}+20{\cdot}4°$ in 5 p.c. alcoholic solution; the *hydrochloride*

$C_9H_{10}O_3N{\cdot}C_2H_5,HCl$

has m.p. 166° (Fischer and Schrauth, Annalen, 1907, 354, 21; Fischer, Ber. 1908, 41, 850, Lilienfeld, Archiv. Physiol. 1894, 383, 555; Röhmann, Ber. 1897, 30, 1978; Fischer, *ibid.* 1901, 34, 433). l-*Tyrosineanhydride* $C_{18}H_{18}O_4N_2$, has m.p. 277°–280° (corr.), $[\alpha]_D^{20}-223{\cdot}8°$ in N/1 sodium hydroxide (Fischer and Schrauth). l-*Tyrosineamide* $C_8H_{10}ON{\cdot}CONH_2$ has m.p. 153°–154° and $[\alpha]_D^{20}+19{\cdot}47°$, condenses readily with ethyl chlorocarbonate to form the *monocarbethoxyl* $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH{\cdot}CO_2Et)CONH_2$, m.p. 155°–157°, and the *dicarbethoxyl*

$EtO_2C{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH{\cdot}CO_2Et){\cdot}CO{\cdot}NH_2$

m.p. 185° (corr.). derivatives; the *dinaphthalenesulphonyl derivative* $C_{29}H_{24}O_6N_2S_2$ has m.p. 204° (corr.) (Koenigs and Mylo, Ber. 1908, 41, 4427).

The following *acyl* derivatives of *l*-tyrosine are described: the *benzoyl*

$HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H)NH{\cdot}COC_6H_5$,

m.p. 165°–166° (corr.) $[\alpha]_D^{20}+19{\cdot}25°$ in 8 p.c. alkali solution, the *brucine* salt is crystalline; the *dibenzoyl*

$C_6H_5CO{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H)NH{\cdot}COC_6H_5$

has m.p. 211°–212° and forms a *potassium* and a *cadmium* salt (Fischer, Ber. 1899, 32, 3638, 2454); the *formyl*

$HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H)NH{\cdot}CHO,H_2O$,

m.p. 171°–174° (corr.) $[\alpha]_D^{20}+84{\cdot}8°$ in 6 p.c. alcoholic solution (Fischer, *ibid.* 1907, 40, 3704); the *palmityl*

$HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H)NH{\cdot}CO[CH_2]_{14}CH_3$

m.p. 133° $[\alpha]_D^{20}+24{\cdot}35$ in 1·8 p.c. alcoholic solution; *palmityl*-l-*tyrosine-palmitylether* $C_{41}H_{71}O_5N$, m.p. 95°–96° $[\alpha]_D^{20}+15{\cdot}28°$ in 1·7 p.c. alcoholic solution; *stearyl*-l-*tyrosine-stearylether*

$C_{45}H_{79}O_5N$,

m.p. 98°–108° (Abderhalden and Funk, Zeitsch. physiol. Chem. 1910, 65, 61); the *β-naphthalenesulphonyl* derivative forms a *hydrochloride* $C_{19}H_{18}O_5NSCl$, m.p. 170°, a *sodium* salt

$C_{19}H_{16}O_5NSNa$

that decomposes at 175°, an *ethyl* ester

$C_{21}H_{21}O_5NS$,

m.p. 140°–143° (Abderhalden and Funk, *ibid.* 1910, 64, 436); the *di-β-naphthalenesulphonyl* derivative

$C_{10}H_7SO_2{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H)NH{\cdot}SO_2C_{10}H_7$

m.p. about 120°, forms a *sodium*

$C_{29}H_{22}O_7NS_2Na$,

m.p. 252°–254°, an *ammonium* and a *barium* salt (Fischer and Bergel, Ber. 1903, 36, 2592); the *phenylisocyanate* derivative

$HO{\cdot}C_6H_4,CH_2{\cdot}CH(CO_2H)NH{\cdot}CONH{\cdot}C_6H_5$,

has m.p. 104°, and forms a *barium*

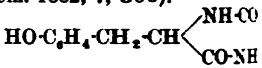
$(C_{16}H_{15}O_4N_2)_2Ba,6H_2O$

and a *silver* salt $C_{16}H_{15}O_4N_2Ag,H_2O$ (Paal and Zitelmann, *ibid.* 1903, 36, 3337); the *α-naphthylisocyanate* derivative melts at 205°–206° (Neuberg and Manasse, *ibid.* 1905, 38, 2359).

dl-*Tryosinylcarbamide*

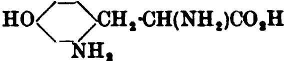
$CO[NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}C_6H_4{\cdot}OH]_2$

decomposes at 240° (Hugounenq and Morel, Compt. rend. 1906, 142, 48); l-*tyrosinhydantoic acid* $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H)NH{\cdot}CONH_2$, m.p. 218°, forms a crystalline silver salt (Jaffe, Zeitsch. physiol. Chem. 1882, 7, 306).



l-*Tyrosinehydantoin* $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{<}\begin{matrix}NH{\cdot}CO\\CO{\cdot}NH\end{matrix}$ melts and decomposes at 242°–245° (Blendermann, *l.c.*).

The alkaloid *surinamine* or *geoffroyine* from geoffroya bark is a *methyltyrosine*, in which the methyl has replaced one of the hydrogens of the amino group (Hiller-Bombien, Arch. Pharm. 230, 513; Blau, Zeitsch. physiol. Chem. 1908, 58, 153; Walpole, Chem. Soc. Trans. 1910, 97, 94).



Derivatives of *l*-tyrosine containing substituents in the aromatic neucleus are: *nitrotyrosine* $C_9H_{10}O_3N{\cdot}NO_2$, obtained by nitration of *l*-tyrosine, forms yellow needles, m.p. 220°; it is optically inactive and is a mixture of the *o*- and *m*- compounds. The *barium* and *silver salts* have been prepared, also the *hydrochloride*, *nitrate* and *sulphate* (Strecker, Annalen, 1850, 73, 70; Casimir Funk, Chem. Soc. Trans. 1912, 1004). *Aminotyrosine* $C_9H_{10}O_3N{\cdot}NH_2$, prepared by reducing nitrotyrosine, forms grey crystals, m.p. 265°, and is a mixture of the *o*- and *m*-isomerides; by the action of nitrous acid the *o*- compound is destroyed and 2-*aminotyrosine* is left; it forms yellow needles, m.p. 273°, and yields a *tribenzoyl* derivative, m.p. 192°–195° (Casimir Funk, *l.c.*). *Dinitrotyrosine* $C_9H_9O_3N(NO_2)_2$, golden yellow crystalline plates, the *calcium*, *barium*, *potassium*, *sodium*, *ammonium*, *magnesium*, *lead*, and *silver* salts have been prepared (Staedeler, Annalen, 1860. 116, 64).

Tyrosinesulphonic acid

$C_9H_{10}(SO_3H)_3NO,2H_2O$

is strongly acidic and gives a beautiful violet colour with ferric chloride. The *ammonium*, *calcium* and *barium* salts are described (Staedeler, *l.c.*).

3-*Bromotyrosine*

$HO{\cdot}C_6H_3Br{\cdot}CH_2{\cdot}CH(NH_2)CO_2H,H_2O$

has a sweet taste, decomposes at 247°–248°; the *hydrobromide* decomposes at 190°–191°, the *picrate* and *platinichloride* are very soluble in water (Johnson and Bengis, J. Amer. Chem. Soc. 1912, 34, 1061); *dibromotyrosine* (probably the 3 : 5 compound) $C_9H_9O_3NBr_2,2H_2O$ obtained by direct bromination of tyrosine, forms fine needles or rhombic plates, dissolves in 218 parts of water at 16° or 26 parts of boiling water: the *silver* salt, the *hydrochloride*, *hydrobromide* and *sulphate* are crystalline, and it forms an unstable *perbromide* (Gorup-Besanez, Annalen, 1863, 125, 281; Millar, Trans. Guinness Lab. 1903, I. Part 1).

3 : 5-*Dichlorotyrosine*, m.p. 252° (decomp.), prepared by chlorinating tyrosinehydantoin and decomposing with barium hydroxide the resulting 3 : 5-*dichlorotyrosinehydantoin*; the *hydrochloride* has m.p. 260°–265° (Wheeler, Hoffmann and Johnson, J. Biol. Chem. 1911, 10, 147).

3 : 5-*Di-iodotyrosine, iodogorgonic acid*

$HO{\cdot}C_6H_2I_2{\cdot}CH_2{\cdot}CH(NH_2)CO_2H$

is not found free in nature but is one of the constituent amino acids of certain proteids; it was first obtained by Dreschel (Zeitsch. Biol. 1896, 33, 85) from *gorgonin*, derived from the horny skeleton of *Gorgonia cavolinii*. This, on hydrolysis with barium hydroxide, yielded an iodo amino acid, hence name *iodogorgonic acid*. It was shown by Wheeler and Jamieson (Amer. Chem. J. 1905, 33, 365) that iodogorgonic acid is a di-iodotyrosine and can be prepared by the direct action of iodine on tyrosine. That it is the 3 : 5-di-iodotyrosine was shown later by Wheeler and Johns (*ibid.* 1910, 43, 11), for on treatment with methyl iodide and potassium hydroxide it yields the methylether of a di-iodotyrosinetrimethylammonium iodide

$MeO{\cdot}C_6H_2I_2{\cdot}CH_2{\cdot}CH(CO_2H)NMe_3I$,

which on boiling with sodium hydroxide yields 3 : 5-diiodo-*p*-methoxylcinnamate. Iodogorgonic acid occurs in a large number of proteids, and has been isolated from *iodo-albacid*, *iodoglidin*, *iodocasein*, *gorgonin* and *spongin* (Oswald, Zeitsch. physiol. Chem. 1911, 70, 310; 71, 200; 74, 290; 75, 353).

3 : 5-*Di-iodo-d,l-tyrosine*, prepared by hydrolysis of the above-mentioned proteids, crystallises from hot water in glassy right-angled plates, from alcohol in hexagonal plates, dissolves in 2164 parts of water at 15°, melts and decomposes at 200°.

3 : 5-*Di-iodo-*l*-tyrosine*, prepared by the action of iodine on *l*-tyrosine, melts at 204° (Oswald), 196°–205° with decomposition (Wheeler and Jamieson); it has $[\alpha]_D^{20}+2{\cdot}27°$ in 4·5 p.c. solution of 25 p.c. ammonia (Abderhalden and Guggenheim, Zeitsch. physiol. Chem. 1907, 54, 331). The *hydrochloride*

$C_9H_9O_3NI_2,HCl$

forms colourless needles, decomposed by water; the *sulphate* $C_9H_9O_3NI_2,H_2SO_4$ is readily soluble; the *silver salt* $C_9H_7O_3NI_2Ag_2$ and *copper salt* $(C_9H_8O_3NI_2)_2Cu,H_2O$ form amorphous precipitates. The *acetyl* derivative

$C_{11}H_{11}O_4NI_2$

decomposes at 225° (Wheeler and Jamieson, Amer. Chem. J. 1905, 33. 365). The *methyl ester* $C_6H_2OI_2{\cdot}CH_2{\cdot}CH(NH_2)CO_2Me$ decomposes at 192°; its *hydrochloride* forms colourless needles that decompose at 211° (corr.), and yields the *nitrate* on treatment with dilute nitric acid (Abderhalden and Guggenheim, Ber. 1908, 41, 1237). *Palmityl*-3 : 5-*di-iodo-tyrosinepalmityl ether* $C_{44}H_{69}O_5NI_2$ melts at 55°–62° (Abderhalden and Slavu, Zeitsch. physiol. Chem. 1909, 61, 405).

A full account of the chemistry and physiology of tyrosine will be found in Biochemisches Handlexikon, von Abderhalden, vol. iv. part 2, 681–702. M. A. W.

U

UARANA *v.* GUARANA.

ULEXITE (*Boronatrocalcit* of G. L. Ulex, 1849; *Natroborocalcite*). A hydrated borate of sodium and calcium $NaCaB_5O_9,8H_2O$, containing 43·0 p.c. B_2O_3. It forms rounded, white masses, 2–3 ins. in diameter, consisting of a loose aggregates of fine, silky fibres; hence the popular name 'cotton-ball.' It occurs abundantly in the borate deposits of Nevada and California, and forms the main mass of those near Iquique in Chile, and in Jujuy province in Argentina. L. J. S.

ULTRAMARINE. Ultramarine was first artificially made on a commercial scale in 1828, by Guimet, who earned the prize of 6000 francs offered by the 'Société d'Encouragement' of France for its production at a cost not exceeding 90*s.* per lb. About the same time, Gmelin (Ann. Chim. Phys. 1828, [ii.] 37, 409) independently discovered how to prepare ultramarine on a laboratory scale. According to Heintze (J. pr. Chem. 1891, [ii.] 43, 98), ultramarine was being made by Kottig, director of the laboratory of the Konigl. Porzellan-manufaktur in Meissen, at the time when Guimet and Gmelin were claiming the priority of the discovery.

Until 1828 ultramarine was obtained by powdering and washing *lapis-lazuli* (*q.v.*); its composition was first determined by Clément and Désormes (Ann. Chim. Phys. 1806, [i.] 57, 317).

Properties.—Artificial *ultramarine blue* occurs in commerce as a bright, azure blue, impalpable powder, insoluble in water. Its constituent elements are sodium, aluminium, silicon, sulphur, and oxygen. Heated to 200°–300° with water in a sealed tube, it leaves a colourless residue free from sulphur, while sodium sulphide passes into solution. It also loses its sulphur when heated with mercuric oxide (Chabrié and Levallois, Compt. rend. 1906, 143, 222). Ultramarine is quite stable towards alkalis, but is readily decomposed by dilute acids, some sulphur being precipitated and hydrogen sulphide evolved. The preceding reactions seem to indicate the presence of some kind of polysulphide in ultramarine; but it is unaltered by concentrated and fuming sulphuric acid, and also by a mixture of glacial acetic acid and acetic anhydride (Hofmann and Metzener, Ber. 1905, 38, 2482), reagents which instantly decompose polysulphides and thiosulphates. Ultramarine withstands a red heat fairly well, although it loses its brilliancy, and becomes greenish; hence it is difficult to imagine that the blue colour is due to free sulphur, as has been suggested (Paterno and Mazzucchelli, Atti. R. Accad. Lincei, 1907, [v.] 16, i. 465). Ultramarine blue becomes brownish-yellow when strongly heated in hydrogen, and violet when heated to dull redness in chlorine. It possesses hydraulic properties and increases the binding power of cement (Rohland, Zeitsch. angew. Chem. 1904, 17, 609).

When heated with aqueous silver nitrate at 120°–140° in a sealed tube for 15 hours, no silver sulphide is produced, but a dark yellow *silver ultramarine* is obtained, together with silver nitrite and other products (Unger, Dingl.

poly. J. 1874, 212, 232; Heumann, Ber. 1877, 10, 991, 1345, 1888; 1879, 12, 60, 784; Bull. Soc. chim. 1877, [ii.] 28, 570; 1878, 30, 326, 327; 1880, 33, 60, 302; Annalen, 1879, 199, 253; 1880, 201, 262; Philipp, Ber. 1877, 10, 1227; Forcrand and Ballin, Bull. Soc. chim. 1878, [ii.] 30, 112; Chabrié and Levallois, *l.c.*). Silver ultramarine is produced by replacement of the sodium in ordinary ultramarine by silver; when fused with various metallic chlorides or iodides, the silver is replaced by other metals, and in this way have been obtained *potassium* (blue), *lithium* (blue), *barium* (yellowish-brown), *zinc* (violet), *manganese* (grey), *ultramarines*, &c. Heated with the requisite organic iodide, silver ultramarine is decomposed, yielding *ethyl*, *amyl*, *benzyl*, and *phenyl ultramarines*, and silver iodide (Forcrand, Compt. rend. 1879, 88, 30; Bull. Soc. chim. 1879, [ii.] 31, 161). These substances regenerate ultramarine when heated with sodium chloride. They do not evolve hydrogen sulphide when treated with cold hydrochloric acid (Chabrié and Levallois, *l.c.*). *Selenium* and *tellurium* ultramarines have also been produced, in which sulphur is substituted by either selenium or tellurium (Guimet, Ann. Chim. Phys. 1878, [v.] 13, 102; Plicque, Bull. Soc. chim. 1877, [ii.] 28, 518; 1878, 29, 522; 1878, 30, 51; Morel, *ibid.* 28, 522). Light blue *boron ultramarine* has been prepared by fusing together anhydrous borax, boric oxide, and either sodium or potassium sulphide, sulphite, or thiosulphate (Hofmann, Zeitsch. angew. Chem. 1906, 19, 1089; 1907, 20, 568; Chem. Ind. 1911, 34, 699).

Ultramarine blue crystallises in the regular system, isomorphous with the minerals *hauyn*, *sodalite*, and *nosean*.

Green ultramarine is formed as an intermediate product in the manufacture of ultramarine blue, and is converted into the latter by roasting with sulphur. According to Philipp (Ber. 1876, 9, 1109), sulphur is not taken up in the change from green to blue, which can be effected by heating with water in a sealed tube at 100°; a small amount of sodium compound is removed by the water. Heated in chlorine, green ultramarine turns bluish-violet; sodium sulphide solution turns it grey.

White ultramarine is obtained by completely excluding air during the roasting of the materials in the manufacture of ultramarine, and is converted into blue ultramarine when heated in either chlorine, oxygen, or sulphur dioxide (Philipp, Ber. 1876, 9, 1109; 1877, 10, 1227; Böttinger, Annalen, 1876, 182, 311; Hofmann, *ibid.* 1878, 194, 1).

Red ultramarine was first obtained by Scheffer in the course of preparing the ordinary substance, by heating the materials very strongly in a muffle freely exposed to air; it contains less sodium and more aluminium than the blue variety (Scheffer, Ber. 1873, 6, 1450; Büchner, Dingl. poly. J. 1879, 231, 446; Zettner, Ber. 1875, 8, 259, 353).

Red ultramarine has been prepared by passing chlorine and steam over heated ultramarine blue.

Yellow ultramarine is obtained by heating the red variety in air for a short time at 360°, or at a little higher temperature (Hofmann, Annalen, 1878, 194, 1). According to Büchner (Ber. 1874, 7, 990), both the yellow and red forms are produced by heating blue ultramarine to 300°–400° in oxygen or sulphur dioxide; the colour changes to red and then to yellow. If chlorine is passed over ultramarine before the formation of the blue variety is completed, at 410°, the colour goes green and then reddish-yellow (Zettner, Ber. 1875, 8, 259, 353).

Violet ultramarine is obtained when the reddish-yellow product previously mentioned is heated with sodium hydroxide (Zettner, *l.c.*). It becomes blue when heated to dull redness or when further heated with an alkali hydroxide, and nitric acid vapours turn it red.

The violet variety was first prepared by Leykauf in 1859 by allowing moist calcium chloride to react with warm ultramarine blue. In 1872 Wunder prepared it by heating the blue form in chlorine at 300° and treating the product with water. It has been manufactured from ultramarine blue by heating the latter, in thin layers, on earthenware trays at 280°, and passing steam over it to remove sulphur. The temperature was then lowered to 160°, and a mixture of chlorine and steam led over it for 3 hours. For further details, and other methods, v. Wunder, Chem. Zeit. 1890, 14, 1119.

Composition.—The various varieties of ultramarine have not yet been satisfactorily shown to possess uniform compositions. In fact, commercial blue ultramarines are manufactured in three different grades, containing different proportions of silica and sulphur. Moreover, it is not possible to obtain products of identical composition even when, in repeated operations, the relative amounts of the different raw materials are maintained constant and the working conditions duplicated as exactly as possible. The following analyses of different samples of ultramarine blue rich in silica indicate its variable composition :—

	Rawlins			Parry and Coste		
	1	2	3	4	5	6
H_2O .	—	—	—	—	—	0·7
SiO_2 .	38·9	39·6	42·7	42·3	41·7	42·4
Al_2O_3 .	29·5	24·0	24·5	26·8	25·2	24·0
Na_2O .	21·0	19·2	20·0	19·5	18·8	18·7
S . .	10·8	13·1	13·0	12·0	14·2	15·4

The differences in composition between ultramarines of different colours are shown by the following numbers, taken from Jordan (Zeitsch. angew. Chem. 1893, 684) :—

	White (Hofmann)	Green (Philipp)	Blue (Philipp)	Blue (Philipp)	Violet (Wunder)	Red (Wunder)	Light blue (Wunder)
Na	21·5	17·02	15·66	14·66	11·7	8·1	11·9
Al .	16·6	15·81	15·39	12·55	13·1	13·3	13·1
Si .	17·0	17·51	16·87	17·29	19·4	19·3	19·7
S .	6·4	7·91	5·69	11·38	13·3	15·2	12·7
O .	38·4	—	—	—	42·1	43·4	42·0
H .	—	—	—	—	0·4	0·7	0·6

The two analyses of ultramarine blue (Philipp in the table refer to the varieties poor and rich in silica respectively.

The *constitution* of ultramarine is naturally a matter of great uncertainty, in view of what has been said concerning its composition. It is commonly regarded as a combined silicate and polysulphide of sodium and aluminium, but objections to this idea have already been mentioned. For the numerous formulæ that have been proposed for ultramarines, *v.* Rawlins, J. Soc. Chem. Ind. 1887, 6, 791; Szilasi, Annalen, 1889, 251, 97; Guckelberger, *ibid.* 1882, 215, 182; Dingl. poly. J. 1883, 247, 343; Clarke, Amer. Chem. J. 1888, 10, 126; Brögger and Bäckström, Jahresber. Tech. 1891, 454; Rohland, Zeitsch. angew. Chem. 1904, 17, 609; Abegg's Handbuch der Anorganischen Chemie, vol. iii. pt. i.

The similarity in composition exhibited by ultramarines of quite different colours suggests that the actual colouring material may represent only a small fraction of the total mass; it has been supposed that such a small amount of a coloured substance is present, disseminated throughout a colourless body in a state of solid solution (Rohland, *l.c.*). Hofmann (Chem. Zeit. 1910, 34, 823) has suggested that this coloured substance is sulphur; the comparative stability of ultramarine at a red heat does not lend support to this assumption. It is noteworthy, however, that were it not for the presence of sulphur, ultramarine would be expected to be colourless.

Uses.—Ultramarine is extensively used in a variety of manufactures. Its large consumption is due to two characteristics: brilliancy as a body colour, and high colouring power. As a body colour it is used in calico-printing, and wall-paper printing, for colouring writing paper and printing-ink, preparing blue pigments, and blueing mottled soap. As a 'whitening' agent it is very valuable, its great strength and purity of tone correcting the yellow tinge in writing and printing papers, cotton and linen goods, paper pulp, whitewash, soap, starch, and even sugar. It is extensively used in the manufacture of square and ball blue for laundry use.

Tests and analysis. (i.) Dilute 0·1 grm. of a standard sample of ultramarine with 0·6 grm. of pure powdered chalk, and determine the amount of chalk that must be added to 0·1 grm. of the sample under examination in order to match the colour of the diluted standard; this gives an indication of the value of the sample. (ii.) Heat a sample in hydrogen to 400°. A good ultramarine becomes grey and then green, the change taking about half an hour; a bad specimen changes in a few minutes. (iii.) Stir a little of the powder under examination in a cold saturated solution of alum, and note the length of time required for decolorisation; compare with a standard sample ground equally fine. (iv.) Shake up with water and alcohol to detect adulteration with coal-tar dyes.

For the quantitative analysis, the substance may be treated as a silicate readily attacked by dilute hydrochloric acid (*v.* ANALYSIS); in the filtrate from the aluminium the sodium may be determined as the sulphate. The determination of sulphur should be effected on a separate portion, by oxidation to sulphuric acid with *aqua regia* or fuming nitric acid, and subsequent estimation as barium sulphate. *See* also Andrews, Analyst, 1910, 35, 157.

MANUFACTURE OF ULTRAMARINE.

The only ultramarines prepared on a large scale are the blue and green sodium-sulphur ultramarines. Three chief varieties of ultramarine blue are found in commerce:—

Glauber salt or *sulphate ultramarine*, the palest variety. It has a slight greenish tinge, small covering power, and is the form most readily attacked by alum.

Soda ultramarine low in sulphur, a pure blue variety, darker than the preceding, and having more covering power.

Soda ultramarine rich in sulphur and silica, the darkest variety, with a reddish tinge. It has high covering power, and is the form most resistant towards alum; consequently it finds extensive use in paper blueing.

Ultramarine is produced when aluminium silicate is calcined with sodium sulphide; the silicate is employed in the form of china clay, or a similar material, with the addition of silica if necessary; sodium sulphide is produced during the manufacture, either from sodium carbonate, carbon, and sulphur, or from sodium sulphate, carbon, and sulphur. The relative proportions of the ingredients is an important factor in the manufacture of ultramarine, but different authorities recommend different mixtures. With materials of the best quality, the following mixtures are said to be the best for producing the three varieties mentioned above:—

Ultramarine blue	Pale	Medium	Dark
China clay . .	100	100	100
Soda . . .	9	100	103
Glauber salt .	120	0	0
Carbon . . .	25	12	4
Silica (Kieselguhr) .	0	0	16
Sulphur . . .	16	60	117

If the clay employed differs in composition from china clay, the relative proportions of clay and silica must, of course, be suitably adjusted.

The manufacture of ultramarine blue is carried out either by (i.) the *direct* or (ii.) the *indirect* process. All ultramarines rich in silica and a certain amount of the other varieties poorer in silica are made by the former method; but the majority of the ultramarines poor in silica are prepared by the latter method, in which ultramarine green is formed as an intermediate product. Both these are dry processes; wet methods have been described and patented, but do not seem to have been adopted on a large scale (Knapp, J. pr. Chem. 1885, [ii.] 32, 375; 1888, 38, 48; McIvor, Eng. Pat. 9200, 1890; McIvor and Cruickshank, Eng. Pat. 19411, 1892).

For general accounts of the manufacture of ultramarine, *v.* Rawlins, J. Soc. Chem. Ind. 1887, 6, 791; Pichot and Grangier, *ibid.* 1888, 7, 573; Röhrig, Chem. Zeit. 1883, 567; Wunder, *ibid.* 1890, 14, 1119; Jordan, Zeitsch. angew. Chem. 1893, 684.

Raw materials.—*China clay*, and French, German, and Bohemian *pottery clays* are used, and always require levigation. The clay must be very finely divided, and free from excessive amounts of iron and manganese oxides. For *soda*, the best soda ash, known as carbonated ash, is employed; it must be stored in a dry place. The *Glauber salt* must be free from acid and iron, and well calcined; it should be ground in stone edge-runner mills before use. Rod or stick *sulphur*, containing very little non-volatile matter, is usually employed, since poorer forms of sulphur produce dirty shades of colour; like the Glauber salt, it is reduced to a fine powder before use. *Carbon* should not contain more than 4 p.c. of moisture; that made from pine trunks is preferred, and is ground in ball mills and stored in a dry place. Charcoal is sometimes replaced by pitch, tar, colophony, &c. If coal is used, it must be of good quality, and free from sand, stones, and pyrites. *Silica* is usually employed in the form of kieselguhr, but sometimes quartz is used; the latter is ignited and then quenched in water to cause it to break up, being finally dried and ground to powder. Silicious carbon, such as charred rice husks, may partly or wholly replace the carbon and silica (Cross, Eng. Pat. 5174, 1903).

Direct process. The formation of ultramarine blue by this process is effected by roasting the well-mixed raw materials, allowing access of air during the operation. The successive operations involved are mixing, roasting, lixiviating, wet-grinding, levigating, pressing, drying, and sifting.

The most intimate and cheapest mixture is obtained when the various raw materials have been ground first in edge-runner mills, and then in balance mills. With mixtures containing much sulphur, the other ingredients should first be well mixed, the sulphur then added, and further mixing effected. The mixtures should, in any case, be calcined as soon as they are prepared.

The 'mass' oven, so called from the mixture being treated in a mass, produces directly very good ultramarine if carefully managed. Fig. 1 gives an idea of the arrangement. The raw materials, well mixed and ground, are shovelled on to the floor of the oven, pushed up to the end with a broad rake, and, after being piled up to nearly the level of the bridge, are nearly flattened, and covered with thin tiles, the joints being filled in with a very thin mortar made with china clay and sand. The oven having been thus filled with about 1 ton of raw material, the front is built up, leaving a hole just above the level of the tiles for observation, fitted with a loose brick. A small hole below this and about opposite the centre of the mass, fitted with a clay stopper, affords a means of taking samples as the burning proceeds. The heat is slowly raised to a bright red, and as it rises small jets of sulphur dioxide are seen to come from the cracks between the covering tiles and burn with feathery flames, increasing in length as the heat becomes greater, and gradually dying away as the reaction is completed. The heat is maintained at its highest point for from 12 to 18 hours, or until the process appears to be finished, when a sample is taken through the small hole by means of a long auger inserted right into the middle of the mass. The sample presents, if sufficiently burnt, a greenish-blue appearance, gives off sulphur dioxide freely without actually burning, and on being spre upon a clean tile quickly loses its heat, an appears a blue colour with a tinge of gree The changes experienced by the mixture ar interesting and remarkable. As introduced it i a yellowish-grey, and becomes successively brow green, and blue. The brown, a dark rich colou is very unstable, and burns on exposure to ai to a greenish half-formed ultramarine, and. eve if not exposed, slow combustion goes on unti oxidation has taken place. The green is almos equally unstable.

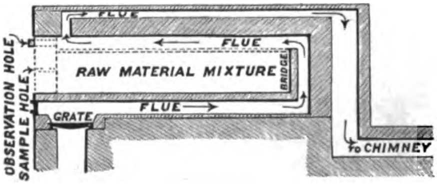


Fig. 1.

When the drawn sample is found to b sufficiently burnt, the operation is concluded b closing the oven, plastering up cracks, an excluding the air as far as possible. It is the left to cool down, which takes a week or 10 days On opening, the mass should appear dark blu the bottom portion not being quite equal i brilliancy to the top owing to the greater degre of heat to which it has been subjected. A los of about one-third of the original weight occurs and the mass shrinks considerably.

Charges amounting to 5 tons are treated in stone troughs, 17–20 ft. long and 10–13 ft. wide, placed in a furnace in such a way that they can be reached on all sides by the flame. The troughs are filled to a depth of 12–16 ins. covered with firebricks, and calcined for about 3 weeks.

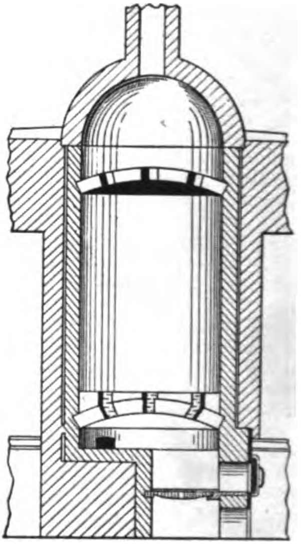


Fig. 2.

Ultramarine blue is also prepared directly in shaft furnaces (Fig. 2), described later on (p. 583). Various special furnaces have been patented (Fr. Pats. 410055, 1909; 407089, 403247, 399211, 400103, 1908; 403077, 1909; 425585, 1910).

A rapid process for the direct preparation of the blue has been patented (Fr. Pats. 391779, 391780, 1908). A mixture of china clay (35 parts), carbon (10 parts), sodium alum (40 parts), rosin (8 parts), and sulphur (7 parts) is heated rapidly to 600°–700°, and maintained at that temperature for about 3 hours; the temperature is then raised to 900°, and the mass stirred well for an hour to oxidise it. Powdered sodium chlorate is then added and the mass stirred for 15 mins.; a further 30 mins. heating then follows. Ultramarine of very superior quality is said to be thus obtained.

Curtius has patented a continuous process. Cast-iron retorts, similar to gas retorts, are employed, lined inside with fire-proof cement. They are set in brickwork, and connected with flues for removing the gases and receivers for condensing sulphur vapour. The charged retorts are closed back and front, but arrangement is made for the admission of air from behind, in order to quickly convert the green ultramarine initially formed into blue. In a modified form of the process, green ultramarine is first produced, discharged into brickwork receptacles beneath the retorts, and directly oxidised to blue (Eng. Pat. 18527, 1890).

The lixiviating, &c. is described later (p. 584).

Indirect process.—The successive stages in this process are mixing, calcining for ultramarine green, crushing, roasting to ultramarine blue, and lixiviating, &c., as in the direct process.

The preparation of the ultramarine green is carried out in either a *crucible* furnace or a *shaft* furnace. The former is a kind of muffle furnace, similar to those used in porcelain works, of square (seldom round) section and lined with firebrick. The ground mixture is filled into tapered crucibles of 12–16 ins. high, the lids are fixed on with a mortar of clay, and the crucibles piled in regular rows in the furnace. A furnace will hold several hundred crucibles, the aggregate charge being 6–8 cwt. of mixture. The temperature is slowly raised until the crucibles are at a bright-red heat, and this temperature is then maintained until the formation of ultramarine green is completed; from 7 to 10 hours are required. It is essential to maintain a uniform temperature throughout the furnace.

When the reaction is finished all openings into the furnace are shut tightly and the furnace allowed to cool down, a process that takes several days.

Shaft furnaces are used for calcining larger quantities, up to 2 tons, of material. These are large, cylindrical, vertical furnaces, lined with firebrick. The furnace is situated at the bottom of the shaft; it is covered in by a firebrick vault, the flat top of which forms the floor upon which the bottom layer of crucibles rests. Numerous openings in the vault allow the heating gases from the furnace to pass up into the shaft. The shaft is filled with crucibles charged with the ground mixture, and arranged layer upon layer. Another vault forms the roof of the shaft proper, and through openings in this the gases pass into a dome and thence into the chimney. Fig. 2 shows such a furnace. These furnaces possess many advantages; they require no special fuel, accommodate large charges and permit the heat to be equally distributed in a very satisfactory manner. Soda mixtures low in sulphur must be heated slowly at first in these furnaces, a bright-red heat being only attained in 4 hours.

The green ultramarine thus produced exhibits a blue tinge on the surface, and if required to be sold as such, the blue outer portions must be removed. This is unnecessary if the product is to be directly converted into blue; it must, however, be crushed and ground to powder.

The material is crushed in roller mills to pieces about the size of peas. Glauber salt greens are then ground in dry mills to a degree of fineness that must be determined by preliminary trials, since if ground beyond a certain degree, the brightness of the final ultramarine blue suffers. Soda greens are much softer than Glauber salt greens, and the application of further pressure during the final grinding must be avoided as much as possible. They are usually ground in ball mills, which may be so constructed as to render the preliminary crushing of the raw green superfluous.

The crushed ultramarine green is converted into blue by roasting it with sulphur; the change is completed in a shorter time by this process than if ammonium chloride, hydrochloric acid, chlorine, &c., are used in the place of sulphur. During the process part of the sodium contained in the green becomes converted into sodium sulphate. Two types of furnace are in extensive use (i.) *cylindrical* or *retort furnaces*, and (ii.) *muffle* furnaces.

The former type consists of an arrangement of strong cast-iron tubes, not exceeding 80 in. long by 16 in. diameter, generally arranged in sets of three, so that the flame entirely surrounds them. They project about 2 in. from the furnace, both at the back and front, and the ends are closed by tight-fitting sheet-iron caps. The arrangement adopted in large works is indicated in Fig. 3; the furnaces are mounted in pairs, back to back. All the gaseous products pass into the narrow corridor A, closed at both ends by doors; through openings in the roof they pass into the flue B, and thence to the chimney.

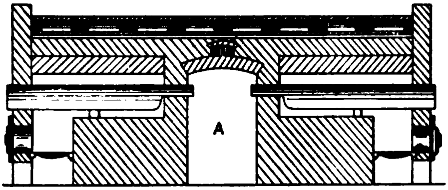


FIG. 3.

In the other type of furnace, the muffle is built into the furnace. The hearth is made of strong fireclay plates with lap joints, luted together, the whole surface being then smoothed. The hearth of the muffle forms the cover of the heating chamber; the products of combustion pass from the grate upwards through flues arranged on the sides of the muffle-walls, thence over the arched roof to the chimney. If the muffle is constructed entirely of fireclay, it is built in completely at the back, and a semicircular hole left in the front, the base of which is on a level with the hearth. This opening, through which the muffle is charged and discharged, can be closed when necessary by a counterpoised iron slide; and since sulphurous gases escape from this opening, it is arched over with a hood for leading these gases to the chimney, an arrangement that is far less convenient and safe than that employed in the cylindrical furnaces. Sometimes the muffle is built with an iron top, and the front of the muffle closed with an iron cap.

The actual roasting process is carried out either (i.) by adding sulphur to the ultramarine green before heating, or (ii.) by heating the green and gradually adding the sulphur during the process. The requisite amount of sulphur is 7 p.c. with soda green, and 9–10 p.c. with Glauber salt green, of the weight of the crude green taken. In carrying out process (i.), the empty retorts or muffles are heated to a medium red heat for soda green, or to bright redness for Glauber salt green. The mixture of green and sulphur is then quickly introduced, and the containing vessels closed. After half an hour, the product is thoroughly mixed and levelled down, a process that is repeated at half-hourly intervals, until all the sulphur has been burnt off. This is indicated by the manner in which the green colour changes to blue. A further 45 mins. heating is given, and then the fire slowly reduced. The retorts and muffles are then tightly closed and allowed to cool. When method (ii.) is employed, the retorts or muffles are charged with ultramarine green, which is raked over and levelled. The successive portions of sulphur added amount to about 1½ lbs. each with retorts (½ cwt. charge), and 4½ lbs. each with muffles (1½ cwt. charge). The first addition of sulphur may be made when a lump of that substance ignites as soon as it is thrown on the ultramarine; the charge is then raked over, and the sulphur allowed to burn away. This operation is repeated until a bright blue product is obtained; samples are withdrawn at intervals and spread out with a steel spatula to examine the colour. The product is then cooled as described under (i.).

The filtering boxes employed in the *lixiviating* process are made of pine, 5–7 ft. long, and 40–60 in. wide. About 6 or 8 in. above the solid bottom a false bottom is mounted, perforated with many ⅜-in. holes, and covered with strong cotton filtering cloth. The cold, calcined ultramarine blue is mixed with a small quantity of hot water (75°–80°) in a vat, thoroughly mixed, and transferred to a filtering box. In this manner all the numerous filtering boxes are charged. The clear filtrates are united, and if sufficiently concentrated (15°B. or more) the liquid is run into crystallising tanks for the recovery of sodium sulphate. Weaker solutions, and the first two or three washings, are concentrated by utilising waste heat from the furnaces. The ultramarine is washed with hot water until quite free from soluble sulphate, of which the crude blue contains about 15 p.c. It is then ground wet in upright mills between hard stones until the requisite fineness is obtained. During this operation sodium silicate passes into solution, and it is therefore necessary to use soft water for the grinding. The whole is then run into a large wooden vat and allowed to settle for 36–48 hours.

The *levigating process* follows next. The top blue liquor is baled out into another vat and left until the extremely finely divided particles of colour have settled; the product is afterwards added to other preparations. The paste remaining in the large vat is distributed in quantities of about 2 cwt. into levigating tanks, three-fourths filled with soft water, and the colour equally distributed throughout the water. The larger particles settle rapidly, and after 2 hours standing the liquids are run into other tanks. The next deposition of ultramarine takes 5 or 6 hours; the liquid is then baled into other tanks, and a further settling of colour for 12 hours is allowed. The liquid now baled off contains extremely finely divided particles: they are precipitated in a fourth series of tanks by the addition of alum, dilute mineral acid, milk of lime or other saline solutions, and the resulting blue paste is pressed. Passing from the first to the fourth series of tanks, the ultramarine becomes successively lighter, finer, bluer, and stronger. The different grades of product are then dried in sheds exposed to air, or on drying hearths heated by waste furnace heat, or in special drying rooms, &c.

The product dries in hard lumps, which must be powdered and sifted; for this purpose ball mills fitted with a continuous sifting device are employed. Very fine brands of ultramarine are sifted in centrifugal sifters or else in a Jasse sifter. It then remains to mix together the various shades and sorts in order to produce the standards of sale; this part of the work is of great importance, as the tinctorial power, fineness of division, depth and purity of colour in each standard, have to be exactly reproduced in bulk.

In making the cheaper brands of ultramarine blue, the pure material is mixed with from 10 to 50 p.c. of gypsum. The latter has an extremely bad effect upon the brightness of certain kinds of ultramarine, which is minimised by incorporating a little glycerol or vaseline into the mixture.

The development of the manufacture of ultramarine has been remarkable. The price in the year of its discovery was about 16*s.* per lb., but competition soon brought this down, and created a demand. Guimet commenced the manufacture in 1828. Between 1830 and 1840 manufactories were established at Cologne and Nuremberg; between 1840 and 1850 nine more were started; 1850–1860 saw nine more; 1860–1870 at least a dozen, and from 1870–1888 four or five, while an equal number of the others had closed down. At the present day (1913) there are about a hundred factories, mainly in Germany and France, although a few are in England, Austria, and the United States, and the annual production of ultramarine is between ten and fifteen thousand tons. The average price is under 30*s.* per cwt.

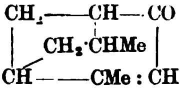
For futher information on ultramarine, *v.* Zerr and Rübencamp's Treatise on Colour Manufacture, translated by Mayer (Griffin & Co.); Bersch's Mineral and Lake Pigments, translated by Wright (Scott, Greenwood & Son); and Hoffmann's Ultramarine (Vieweg u. Sohn, Braunshweig).

ULTRAMARINE, GREEN, *v.* Ultramarine; also Chromium.

ULTRAMARINE, YELLOW. *Barium Chromate v.* Barium; also Chromium.

UMBELLIFERONE *v.* Gum resins.

UMBELLULARIA CALIFORNICA (*Nutt*). An evergreen tree indigenous to California, known locally as 'California Laurel,' 'Mountain Laurel,' 'California Bay-tree,' 'Spice-tree,' 'Pepper-wood,' &c. The essential oil is an aromatic liquid possessing a peculiar pungency due to the presence of a ketone *umbellulone* $C_{10}H_{14}O$



which forms 60 p.c. of the essential oil; the other constituents are eugenol, 1·7 eugenol methyl ether, 10; *l*-pinene, 6·0; cineol 20·0 p.c.; safrole and fatty acids, traces (Power and Lees, Chem. Soc. Trans. 1904, 85, 629; Tutin, *ibid.* 1906, 89, 1104; 1908, 93, 252).

UMBELLULIC ACID *v.* Hendecatoic acids.

UMBER. A brown pigment, consisting of a mixture of the hydrated oxides of iron and manganese, mechanically associated with a large proportion of earthy matter of variable character. The material is prepared for the market by grinding and levigation. Raw umber is exported from Cyprus, Turkey, and Italy; while it is also worked to a limited extent in the United States.

Church (The Chemistry of Paints and Painting, 1890) gives the following analysis of a choice sample of raw umber from Cyprus: water, given off at 100°C., 4·8 p.c.; water expelled at a red heat, including organic matter, 8·8; Fe_2O_3, 48·5; MnO_2, 19; CaO, 1·4; MgO, 0·5; Al_2O_3, 2·1; P_2O_5, 0·9; SiO_2, 13·7; CO_2, &c., 0·3. Part of the manganese probably exists as Mn_3O_4.

For other analyses of umbers, siennas, and ochres, *v.* G. H. Hurst in Chem. News. 1889, 59, 172. He found crude Derbyshire umber to yield the following results: hygroscopic water, 13·47 p.c.; combined water, 5·17; $BaSO_4$, 30·10; SiO_2, 4·43; $CaSO_4$, 2·15; $CaCO_3$, 2·61; Al_2O_3, 8·08; Fe_2O_3, 22·50; MnO_2, 11·53. Hurst regards most ochres as alteration products, formed mainly by the oxidation and hydration of pyrites *in situ*, and mechanically mixed with silica, clay, and other earthy matter. Umbers may have been washed as a fine sediment from deposits of iron and manganese ores. The pigment termed *burnt umber* is merely umber which has been exposed to heat, whereby its colour becomes somewhat reddened.

Ref.—G. P. Merrill, The Non-Metallic Minerals, 2nd ed., New York, 1910, 104; *v.* Ochre.

F. W. R.

UNDECATOIC ACIDS and **UNDECYLIC ACID** *v.* Hendecatoic acids.

UPAS ANTIAR *v.* Antiar resin.

UPAS TIEUTE *v.* Nux vomica.

URACIL *v.* Pyrimidines.

URALITE. A name proposed by G. Rose in 1831 for pseudomorphs of hornblende after augite from the Ural Mountains. (For a *résumé* of the literature, *v.* A. Wilmore, Geol. Mag. 1910, [v.] 7, 357.) Also used as a tradename for a preparation of serpentine-asbestos, made into the form of boards for fire-proof partitions (*v.* Asbestos). L. J. S.

URAMIL *v.* Pyrimidines.

URANINITE *v.* Pitchblende.

URANITE. An early name for the 'uranium micas' in use before these had been separated into the species autunite (calco-uranite) and torbernite (cupro-uranite) (*qq.v.*).

URANIUM. Sym. U. At.wt. 238·5. In 1789 Klaproth prepared from *pitchblende* some compounds of a new element, which he called *uranium* (Crell's Ann. 1789, [ii.] 400). The compounds of uranium were studied by Richter, Arfvedson, Berzelius, and others. In 1840 Péligot showed that what had previously been thought to be uranium was really one of its oxides; he prepared the metal by reducing uranous chloride with potassium (Ann. Chim. Phys. 1842, [iii.] 5, 5). The work of Péligot was confirmed and extended by Ebelmen (*ibid.* 1842, [iii.] 5, 189), Wertheim (*ibid.* 1844, [iii.] 11, 49), Rammelsberg (Pogg. Ann. 1842, 55, 318; 56, 125), and Hermann (Ueber einige Uranverbind. Göttingen, 1861).

Occurrence.—Uranium is not very abundant; its chief ore is *pitchblende* or *uraninite*, which consists of impure U_3O_8, and is found in Cornwall, at Joachimsthal (Bohemia), and other localities. It contains from 40 to 90 p.c. of U_3O_8 (Hermann, J. pr. Chem. 1859, [i.] 76, 326; Ebelmen, Ann. Chim. Phys. 1843, [iii.] 8, 498; Whitney, Amer. J. Sci. 1849, [ii.] 7, 434; Genth, *ibid.* 1857, 23, 421; Zimmermann, Annalen, 1886, 232, 300). *Clevite* and *bröggerite* are varieties of pitchblende rich in rare earths. *Carnotite* is a vanadate of potassium and uranium, found in Utah and Colorado (Friedel and Cumenge, Bull. Soc. chim. 1899, [ii.] 21, 328). *Samarskite* is a uranotantalite of iron and yttrium, found in Siberia (Miask) and North Carolina (Rammelsberg, Pogg. Ann. 1877, 160, 658); *fergusonite* is a complex columbate of yttrium, cerium, uranium, calcium, and iron (Rammelsberg, *ibid.* 1873, 150, 200).

Nearly all the phosphates, silicates, and zirconates of the rare earths contain small quantities of uranium, notably *xenotime*, *æschenite*, *columbite*, *cerite*, and *monazite*. *Thorianite* (*v.* Thorium) contains from 10 to 20 p.c. of uranosouranic oxide. *See* also Szilárd, Le Radium, 1909, 6, 233.

Naturally occurring uranium minerals are radioactive; it was from the pitchblende of Joachimsthal that radium was first prepared, whilst helium was originally obtained from clevite.

Treatment of uranium minerals; preparation of uranium. The chief source of uranium compounds is pitchblende, which, after a preliminary roasting, is heated in a reverberatory furnace with sodium carbonate. The product is extracted with warm dilute sulphuric acid and filtered, the residue being used in the preparation of radium salts. The filtrate is worked up commercially for uranium compounds as described under sodium diuranate (p. 588). The following method is due to Wöhler; the liquid is treated with hydrogen sulphide to remove arsenic, antimony, copper, lead, and bismuth, and after oxidising the filtrate with nitric acid, excess of ammonia is added. The washed precipitated iron hydroxide and ammonium uranate are digested at 100° with concentrated ammonium carbonate, containing ammonia in excess, to dissolve the ammonium uranate. The double salt, ammonium uranyl carbonate, crystallises out on cooling the filtered liquid. From the mother liquor a quantity of ammonium uranate can be obtained by precipitating any zinc, nickel, and cobalt with ammonium sulphide, and evaporating the filtrate. Both ammonium uranate and ammonium uranyl carbonate leave the green oxide U_3O_8 when ignited in the air.

Carnotite is fused with potassium hydrogen sulphate and the mass extracted with water; from the solution the double sulphates of uranium and vanadium with potassium sulphate are crystallised out. The crystalline product is reduced with zinc and sulphuric acid, and the vanadium then precipitated with ammonia and ammonium carbonate. From the filtrate the uranium is thrown down as ammonium uranate by boiling (Gin, Chem. Zentr. 1906, ii. 1172; *cf.* Haynes, Mines and Minerals, 1909, 30, No. 3, 139).

Metallic uranium was first prepared by Péligot (*l.c.*) by reducing the tetrachloride with potassium. Zimmermann (Annalen, 1883, 216, 1) replaced the potassium by sodium. It is better to employ the double chloride of uranium and sodium, and magnesium may be used in place of potassium (Moissan, Compt. rend. 1896, 122, 1088). These methods are unsatisfactory, since uranium tetrachloride is extremely hygroscopic. Uranium is best prepared by heating 500 parts of the oxide U_3O_8 with 40 parts of sugar carbon in the electric furnace in a carbon tube. The product, which contains a little carbon, is purified by heating it in a crucible brasqued with uranium oxide, and embedded in another crucible brasqued with titanium, to prevent access of nitrogen to the uranium (Moissan, Compt. rend. 1893, 116, 349). Reduction of uranium dioxide by carbon begins at 1500° (Greenwood, Chem. Soc. Trans. 1908, 93, 1492). The oxides of uranium may also be reduced by heating with aluminium powder (Aloy, Bull. Soc. chim. 1901, [iii.] 25, 153; Stavenhagen, Ber. 1899, 32, 3065; Stavenhagen and Schuchard, *ibid.* 1902, 35, 909; Giolitti and Tavanti, Gazz. chim. ital. 1908, 38, ii. 239). Uranium may also be prepared by the electrolysis of the fused double chloride of uranium and sodium, in an inert atmosphere, using carbon electrodes (Moissan, Compt. rend 1896, 122, 1088); and is obtained in the pyrophoric state by heating its amalgam in a vacuum (Férée, Bull. Soc. chim. 1901, [iii.] 25, 622).

Properties.—Pure uranium is a white metal, which takes a high polish; its density is 18·7, and its specific heat 0·02765 (Zimmermann, Annalen, 1886, 232, 310; Ber. 1882, 15, 851). It melts at a white heat, and can be distilled in the electric furnace (Moissan, Compt. rend. 1906, 142, 425; *cf. ibid.* 1893, 116, 1429; 1896, 122, 1088). The most prominent lines in the emission spectrum are in the yellow (Thalén, Ann. Chim. Phys. 1869, [iv.] 18, 239; Hasselberg, K. Svenska. Vet-Akad. Handl. 1910, 45, 3; Pollok, Sci. Proc. Roy. Dubl. Soc. 1909, 11, 331). Most uranium compounds possess marked absorption spectra (Morton and Bolton, Chem. News. 1873, 28, 47, 113, 164; Jones and Strong, Phil. Mag. 1910, [vi.] 19, 566; Strong, Zeitsch. physikal. Chem. 1910, 11, 668) and are fluorescent, the fluorescence spectra having been studied by E. Becquerel (Ann. Chim. Phys. 1872, [iv.] 27, 539) and H. Becquerel (Compt. rend. 1885, 101, 1252; 1907, 144, 459); *v.* also Becquerel and Kamerlingh-Onnes (*ibid.* 1910, 150, 647) for phosphorescence at low temperatures.

Uranium in the form of powder is unaltered in dry air at ordinary temperatures; it burns in oxygen at 170°. It unites directly with fluorine in the cold, and with chlorine, bromine, and iodine when gently heated. At 500° it combines with sulphur and selenium, and at 1000° unites readily with nitrogen. It forms a crystalline carbide (Moissan, Compt. rend. 1896, 122, 1088).

Uranium powder decomposes water slowly at ordinary temperatures, more rapidly at 100°. It dissolves readily in hydrochloric, sulphuric, and nitric acids.

Uranium is closely allied to the elements chromium, molybdenum, and tungsten; they all exhibit a maximum valency of six, yield acidic trioxides, and form numerous halogen derivatives in which their valencies vary from two to six. These halogen derivatives in general bear little resemblance to well-defined salts, as is indicated by their volatility, solubility in numerous organic media, and the ease with which they are hydrolysed by water. There are two principal series of uranium salts: (i.) the *uranous* compounds, corresponding to the basic oxide UO_2; and (ii.) the *uranyl* compounds, in which the group UO_2 functions as a bivalent metallic radicle. Besides these, there exist *uranates*, *diuranates*, and *peruranates*, analogous to the corresponding chromium derivatives (*v.* O. de Coninck, Bull. Acad. roy. Belg. 1909, 175). The *uranous* salts are usually green or blue, and in solution are readily oxidised to uranyl compounds, even by air, the rate of oxidation being proportional to the concentration of the solution and inversely proportional to the square of the concentration of the hydrogen ions present (McCoy and Bunzel, J. Amer. Chem. Soc. 1909, 31, 367). They are obtained by the reduction of uranyl compounds (*v.* Aloy and Auber, Bull. Soc. chim. 1907, [iv.] 1, 569; Colani, Ann. Chim. Phys. 1907, 12, 59). The *uranyl* salts are generally yellow, with a greenish fluorescence. They are highly sensitive to light, and are employed in photography (Niepce de Saint Victor, Compt. rend. 1858, 46, 448, 489; Titlestad, Zeitsch. physikal. Chem. 1910, 72, 257; Bacon, Philippine J. Sci. 1910, 5, 281). They are somewhat analogous to basic salts, but they are stable in solution, being only hydrolysed to a slight extent. On electrolysis the uranyl ion UO_2 migrates to the cathode. Uranyl salts form numerous complex derivatives, especially with salts of organic acids (Dittrich, Zeitsch. physikal. Chem. 1899, 29, 449; Ley, *ibid.* 1900, 30, 193; Ber. 1900, 33, 2658; Kohlschütter, Annalen, 1900, 311, 1).

Uranium salts are radioactive, emitting *a* rays, and producing a new radioactive element called *Uranium-X* (*v. infra*, Uranium-X and Radioactivity).

Atomic weight. This was taken as *circa* 120 until Mendeléeff pointed out the similarity of uranium to chromium, molybdenum, and tungsten, and proposed the value 240 (Annalen, Suppl. 1872, 8, 178; Chem. News. 1880, 41, 39), which assigned to uranium a position in the Periodic Classification in the same Group as the elements just mentioned. The determination of the specific heat of the metal and the vapour densities of uranous chloride and bromide (Zimmermann, Annalen, 1882, 216, 1) confirmed the views of Mendeléeff. The actual value at present adopted (238·5) rests mainly on the work of Zimmermann (Annalen, 1886, 232, 299), Aloy (Ann. Chim. Phys. 1901, [vii.] 24, 418), and of Richards and Merigold (Proc. Amer. Acad. 1902, 37, 365; Zeitsch. anorg. Chem. 1902, 31, 235).

OXIDES AND OXYACIDS.

Uranium dioxide or *Uranous oxide* UO_2 is obtained by heating the green oxide or uranyl oxalate in a stream of hydrogen (Berzelius, Péligot, Ebelmen); or by electrolysing uranyl nitrate solution (O. de Coninck and Camo, Bull. Acad. Roy. Belg. 1901, 321); these methods yield a brown pyrophoric powder. The reduction of uranyl chloride solution with magnesium or aluminium yields uranous oxide as a black powder (de Coninck, *ibid.* 1909, 744). It is obtained as black, microscopic crystals by reducing crystalline uranic hydroxide in hydrogen (Aloy, Bull. Soc. chim. 1900, [iii.] 23, 368); and as jet black octahedra by fusing the amorphous form with borax, and washing the product with dilute hydrochloric acid (Hillebrand, Zeitsch. anorg. Chem. 1893, 3, 249). It is a basic oxide, and dissolves in concentrated acids to form green uranous salts. It combines directly with chlorine and bromine, forming uranyl chloride and bromine, and burns when heated in air, the green oxide U_3O_8 being produced.

Uranous hydroxide $UO_2,2H_2O$ is precipitated by adding an alkali to a solution of a uranous salt and boiling; it forms black flakes, and readily dissolves in dilute acids (Aloy, Bull. Soc. chim. 1899, [iii.] 21, 613).

Uranium trioxide, *uranic oxide, uranic anhydride,* or *uranyl oxide* UO_3 is a chamois yellow powder, obtained by heating uranyl nitrate to 250°; also by heating the hydroxide or double uranyl ammonium carbonate to 250° (Ebelmen Ann. Chim. Phys. 1842, [iii.] 5, 199; de Coninck, Compt. rend. 1901, 132, 204; Bull. Acad. Roy. Belg. 1904, 363, 448). It oxidises to the green oxide when heated in air, and is reduced by hydrogen to uranous oxide.

This oxide is slightly basic, but only one-third of its oxygen can be replaced by acidic radicles; the salts thus produced are of the type $UO_2R^I_2$, and are called *uranyl* compounds. Towards strong bases, uranic oxide behaves as an acid anhydride, similar to chromic anhydride.

Uranic hydroxide or *uranic acid* UO_3,H_2O is best prepared by heating a solution of uranyl nitrate in alcohol until no more brown fumes are evolved, and washing the yellow precipitate with boiling water (Malaguti, Ann. Chim. Phys. 1843, [iii.] 9, 463). It may also be obtained, mixed with the dihydrate, by evaporating a solution of uranyl nitrate to complete dryness (de Coninck, Compt. rend. 1909, 148, 1462). The *dihydrate* $UO_3,2H_2O$, which is obtained as a yellow precipitate by boiling the double uranyl ammonium carbonate with water, loses water at 100°, and yields the hydroxide UO_3,H_2O (Ebelmen, *l.c.*; for other methods, *v.* Jacquelin, Ann. Chim. Phys. 1842, [iii.] 5, 199; Riban, Compt. rend. 1881, 93, 1140; Aloy, Bull. Soc. chim. 1900, [iii.] 23, 368). Uranic hydroxide has a sp.gr. of 5·9; it does not alter in air, and when heated to 300° it is dehydrated. For the preparation of the colloidal hydroxide, *v.* Szilárd, J. Phys. Chem. 1907, 5, 488, 636.

Uranosouranic oxide or *Green oxide of uranium* $U_3O_8(=UO_2{\cdot}2UO_3)$ occurs more or less pure as *pitchblende.* It can be obtained by heating any of the other oxides to a red heat in air, also by igniting ammonium uranate or any uranium salt of a volatile acid. It forms a dark-green, lustrous powder of sp.gr. 7·2, insoluble in water; in concentrated acids it dissolves, forming a mixture of uranous and uranyl salts. This oxide is employed for producing a black glaze on porcelain. It is radioactive, and has been suggested as a suitable standard of α-ray radioactivity (McCoy and Ashman, Amer. J. Sci. 1908, 26, 521).

A violet hydroxide can be obtained by the action of light on aqueous uranyl oxalate or alcoholic uranyl acetate (*v.* Aloy, Bull. Soc. chim. 1900, [iii.] 23, 368).

Uranium pentoxide $U_2O_5(=UO_2{\cdot}UO_3)$ is formed by the strong ignition of uranium nitrate in air, and is a black powder, used for producing a black glaze on porcelain. According to Zimmermann (Annalen, 1886, 232, 273) it is a mixture of U_3O_8 and UO_2.

Uranium peroxide UO_4 is only known in the hydrated form as *peruranic acid* $UO_4,2H_2O$. It is obtained by adding hydrogen peroxide to a mixture of uranyl and uranous sulphate in aqueous solution, and drying the precipitate over concentrated sulphuric acid (de Coninck, Bull. Acad. Roy. Belg. 1909, 692; *cf.* Fairley, Chem. Soc. Trans. 1877, 31, 133; Zimmermann, Annalen, 1886, 232, 273; Alibegoff, *ibid.* 1886, 233, 123). It forms a yellow powder, which loses oxygen when heated; when treated with alkali hydroxides it yields a mixture of alkali uranate and peruranate.

URANATES.

The alkali uranates are formed by precipitating uranyl salts with alkali hydroxides; those of the other metals by adding ammonia to a mixture of a uranyl and a metallic salt. They are yellow, insoluble in water, but soluble in acids. The majority are of the type $M_2O{\cdot}2UO_3$, analogous to the dichromates (*v.* Drenkmann, J. 1861, 255; Patera, J. pr. Chem. 1850, 51, 125; Debray, Ann. Chim. Phys. 1861, [iii.] 61, 451; Grandeau, *ibid.* 1886, [vi.] 8, 224; Zimmermann, Annalen, 1882, 213, 290; Ditte, Compt. rend. 1882, 95, 988; de Coninck, Bull. Acad. roy. Belg. 1909, 173, 835).

Ammonium uranate. This is obtained as a yellow, voluminous precipitate by adding ammonia to a solution of a uranyl salt. It is prepared by boiling a solution of uranyl sodium carbonate with ammonium sulphate; or by boiling sodium diuranate (*q.v.*) with concentrated ammonium chloride solution, and forms a fine, deep yellow-coloured powder, that is sometimes used commercially, under the name *uranium yellow,* in the preparation of uranium glass (*v.* Stolba, Zeitsch. anal. Chem. 1864, 3, 74, and sodium diuranate).

Potassium uranate K_2UO_7, obtained by fusing uranyl chloride with a mixture of potassium and ammonium chlorides (Zimmermann, *l.c.*), forms yellow, rhombic crystals.

Potassium diuranate $K_2U_2O_7$ is obtained in the form of a trihydrate by precipitating a uranyl salt with potassium hydroxide and drying the product at 100° (Patera, *l.c.*).

Sodium uranate Na_2UO_4 may be obtained by fusing the green oxide with sodium chloride and sodium carbonate (Ditte, *l.c.*; Zimmermann, *l.c.*).

Sodium diuranate $Na_2U_2O_7$ is prepared commercially from pitchblende, which is powdered and roasted to remove the greater part of the sulphur, arsenic, and molybdenum. The ore is then heated in a reverberatory furnace with sodium carbonate and a little sodium nitrate. The product is washed with water, when soluble arsenate, molybdate, tungstate, and vanadate of sodium are removed; sodium uranate is insoluble in water. The insoluble residue is dissolved in dilute sulphuric acid, the solution evaporated to remove excess of acid, diluted and filtered from silica, lead sulphate, and basic sulphate and arsenate of bismuth, and an excess of sodium carbonate solution added. A solution of uranyl sodium carbonate is thus obtained, while the basic carbonates of iron, aluminium, nickel, and cobalt are precipitated and removed. The uranium is then precipitated as sodium diuranate by adding sodium hydroxide, or by neutralising with sulphuric acid and boiling. The yellow precipitate is thoroughly washed, dried, and pulverised (Patera, J. pr. Chem. 1849, [i.] 46, 182; 1850, 51, 122; Giseke, J. 1852, 779; Anthon, J. 1860, 698; Kessler, J. 1857, 199; Hofmann and Strauss, Ber. 1900, 33, 3126; *cf.* Metzger and Heidelberger, J. Amer. Chem. Soc. 1909, 31, 1040).

Sodium diuranate is found in commerce as the hexahydrate $Na_2U_2O_7,6H_2O$. It is a fine yellow powder, known as *uranium yellow*, and is used in painting and staining glass and porcelain, and for making the fluorescent 'uranium glass.'

PERURANATES.

These salts are formed by the action of hydrogen peroxide and alkali hydroxides on uranyl salts, and are usually precipitated by means of alcohol as orange-yellow crystals. The sodium salt has the formula $Na_4UO_8,8H_2O$. These compounds have been studied by Fairley (Chem. Soc. Trans. 1877, 31, 134) and Melikoff and Pissarjewsky (Ber. 1897, 30, 2092; Zeitsch. anorg. Chem. 1898, 18, 59; J. Russ. Phys. Chem. Soc. 1902, 34, 472).

A red potassium peruranate $K_2UO_5,3H_2O$ is obtained when peruranic acid is added to hydrogen peroxide containing alcohol, and the solution treated with potassium hydroxide (Aloy, Bull. Soc. chim. 1903, [iii.] 29, 292). The formation of this substance may be employed as a delicate colorimetric test for the presence of uranium (Aloy, *ibid.* 1902, [iii.] 27, 734).

URANIUM COMPOUNDS.

Uranium tetrafluoride or *Uranous fluoride* UF_4 is the main product of the action of fluorine on uranium. It is prepared by adding hydrogen fluoride to a solution of uranous chloride, and forms a green powder, insoluble in water and dilute acids (Smithells, Chem. Soc. Trans. 1883, 43, 125; Bolton, J. 1886, 209). It leaves a residue of oxide when heated in air; and forms double fluorides with the alkali fluorides.

Uranium hexafluoride UF_6 is best obtained by the action of fluorine on the cooled pentachloride—

$$2UCl_5+5F_2=UF_6+UF_4+5Cl_2.$$

It forms colourless, monoclinic prisms, which sublime at ordinary temperatures under diminished pressure. It melts at 69·2° under a pressure of two atmospheres, and boils at 56·2°. The solid has a density of 4·68; the vapour gives a value 11·7 (air=1). It is very hygroscopic, and highly reactive (Ruff and Heinzelmann, Zeitsch. anorg. Chem. 1911, 72, 63: *cf.* Ber. 1909, 42, 492).

Uranium trichloride UCl_3 is obtained by heating the tetrachloride in hydrogen (Péligot, Ann. Chim. Phys. 1842, 5, 20), and is a reddish-brown substance, which easily dissolves in water, forming a red solution that slowly evolves hydrogen and becomes green.

Uranium tetrachloride or *Uranous chloride* UCl_4 is produced when uranium is heated in chlorine, and is prepared by passing chlorine over heated uranium carbide or a mixture of any oxide of uranium with carbon (Péligot, Annalen, 1842, 43, 258; Zimmermann, *ibid.* 1882, 213, 320; 1883, 216, 8; Roscoe, Chem. Soc. Trans. 1874, [ii.] 12, 933; Aloy, Bull. Soc. chim. 1899, [iii.] 21, 264). It forms dark-green octahedra, is volatile at a red heat, and the vapour has a density (air=1) of 13·33 (Zimmermann). In molten bismuth chloride as solvent the molecular weight is 373 (theory=380·3) (Rügheimer and Gonder, Annalen, 1908, 364, 45). It is extremely deliquescent, fumes in the air, and readily dissolves in water with evolution of heat; the solution is a powerful reducing agent. The solution reacts acid, and on evaporation, leaves an oxychloride. Boiling water completely hydrolyses the chloride.

It forms double chlorides with the chlorides of the alkali and alkaline earth metals (Moissan, Compt. rend. 1896, 122, 1088; Aloy, Bull. Soc. chim. 1899, [ii.] 21, 264).

Uranium pentachloride UCl_5 is obtained by the direct union of the tetrachloride and chlorine. It exists in two forms: (i.) long, dark needles which are green by reflected, and ruby-red by transmitted, light, and (ii.) a light-brown, mobile powder. It is very hygroscopic, and is decomposed by water. It cannot be volatilised without decomposition; in an atmosphere of carbon dioxide, dissociation into the tetrachloride and chlorine is complete at 235° (Roscoe, Chem. Soc. Trans. 1874, 12, 933).

Uranium tetrabromide or *Uranous bromide* UBr_4 is obtained by heating the green oxide of uranium with excess of sugar charcoal, and passing bromine vapour over the heated mixture of uranous oxide and carbon thus produced (Zimmermann, Annalen, 1883, 216, 2; Alibegoff, *ibid.* 1886, 232, 132; Richards and Merigold, Zeitsch. anorg. Chem. 1902, 31, 250). It forms lustrous, dark-brown tablets of sp.gr. 4·838 at 21°/4°. At a red heat it is volatile; the vapour density (air=1) is 19·46 (Zimmermann). It closely resembles the tetrachloride in properties.

Uranium tetraiodide or *Uranous iodide* UI_4 is prepared by passing the vapour of iodine over powdered uranium heated to 500° in the absence of air (Guichard, Compt. rend. 1907, 145, 921). It forms black, crystalline needles, which melt at about 500°, and have a sp.gr. of 5·6. The aqueous solution is dark green and closely resembles the chloride in properties.

Uranous oxyfluoride UOF_2 is obtained by the action of hydrofluoric acid on uranosouranic oxide—

$$U_3O_8+6HF=UOF_2+2UO_2F_2+3H_2O.$$

It is a fine green powder, insoluble in water (Giolitti and Agamennone, Atti. R. Acad. Lincei, 1905, 14, i. 114).

Uranyl fluoride UO_2F_2 is formed in the preceding reaction, and is a yellow soluble mass. It also exists, according to Smithells (Chem. Soc. Trans. 1883, 43, 125) in a white crystalline form, which can be sublimed; this modification is prepared by carefully heating the tetrafluoride in air. It is hygroscopic and forms a yellow solution in water. Both forms unite with potassium fluoride forming a lemon-yellow crystalline double salt $UO_2F_2\cdot3KF$, which can also be obtained from uranyl acetate and an excess of potassium fluoride. This salt is trimorphous (Baker, *ibid.* 1879, 35, 763). The corresponding double salts of other metals are also known, and are converted into deep yellow-coloured peroxyfluorides by hydrogen peroxide Lordkipanidzé, J. Russ. Phys. Chem. Soc. 1900, 32, 283).

Uranyl chloride UO_2Cl_2 is obtained by heating uranous oxide to redness in a stream of chlorine. It is a yellow crystalline mass, stable in dry air; it is reduced by hydrogen at a red heat to the dioxide. Uranous chloride is soluble in water, alcohol, and ether, and its aqueous solution yields the monohydrate UO_2Cl_2,H_2O on evaporation. A solution of uranyl chloride may be prepared by oxidising uranous chloride with nitric acid or by dissolving uranium trioxide in concentrated hydrochloric acid (Mylius and Dietz, Ber. 1901, 34, 2774; de Coninck, Compt. rend. 1909, 148, 1769; Bull. Acad. roy. Belg. 1909, 836). For a table of specific gravities of its aqueous solutions, *v.* de Coninck, Ann. Chim. Phys. 1904, [viii.] 3, 500.

Uranyl bromide UO_2Br_2 may be obtained in an impure state by heating uranous oxide in bromine vapour. It is obtained in aqueous solution by acting on uranous oxide with bromine water, or by dissolving uranic oxide in hydrobromic acid. Yellow needles of the hydrated compound separate on concentrating the solution; they decompose when heated (de Coninck, Bull. Acad. roy. Belg. 1902, 12, 1025).

Uranyl iodide UO_2I_2 is obtained by adding barium iodide in slight excess to an ethereal solution of uranyl nitrate. It separates from ether in red deliquescent crystals, and is not very stable (Aloy, Ann. Chim. Phys. 1901, [vii.] 24, 412).

Uranium monosulphide US is a black, amorphous powder formed by heating the sesquisulphide in hydrogen (Alibegoff, Annalen, 1886, 233, 131, 135).

Uranium sesquisulphide U_2S_3 is a greyish-black substance formed by heating the tribromide of uranium in hydrogen sulphide (Alibegoff, *l.c.*).

Uranium disulphide US_2 is formed by the direct union of its elements at 500° (Moissan); at a higher temperature uranium burns vividly in sulphur vapour. The sulphide is best prepared by heating the double chloride of uranium and sodium in a current of hydrogen laden with the vapour of sulphur; or the double chloride may be fused with sulphide of sodium, aluminium, magnesium, antimony or tin (Colani, Compt. rend. 1903, 137, 382; Ann. Chim. Phys. 1907, [viii.] 12, 59). It forms large, slender, pearly crystals; the amorphous powder, obtained by heating uranous chloride in hydrogen sulphide, is greyish-black in colour. It oxidises in the air to uranyl sulphide, and with nitric acid is rapidly converted into uranyl sulphate.

A black, hydrated disulphide is obtained by precipitating a uranous salt with ammonium sulphide; it rapidly oxidises in the air to uranyl sulphide.

Uranyl sulphide UO_2S is obtained by adding ammonium sulphide to an alcoholic solution of uranyl nitrate, washing the precipitate with alcohol and drying *in vacuô*. By precipitating in aqueous solution a brown hydrated form is obtained (Remelé, Compt. rend. 1864, 58, 716). It rapidly decomposes by heating to 180°; warm water converts it into hydrated uranous oxide and sulphur. It dissolves in dilute acids and in ammonium carbonate. When digested for 48 hours with cold ammonium sulphide exposed to air, a deep-red solid is obtained, soluble in acids with the evolution of hydrogen sulphide and deposition of sulphur. This substance is called *uranium-red* (Patera, J. pr. Chem. 1850, [i.] 51, 122; Remelé, Pogg. Ann. 1865, 124, 158; Hermann, J. 1861, 14; Zimmermann, Annalen, 1880, 204, 204). A complicated substance of the formula $5UO_3\cdot2K_2O\cdot KHS_2,xH_2O$ is obtained by precipitating uranyl nitrate with potassium sulphide and treating the precipitate with potassium carbonate (Kohlschütter, Annalen, 1900, 314, 311). This is also called *uranium-red*; acids decompose it, liberating sulphur and hydrogen sulphide.

Uranyl sulphide is formed in black, tetragonal needles by heating uranosouranic oxide with sulphur and potassium thiocyanate (Milbauer, Zeitsch. anorg. Chem. 1904, 42, 448).

The *oxysulphide* $2US_2\cdot UO_2$ has been described by Hermann (J. 1861, 260).

Uranium selenides USe_2 and U_2Se_3 are obtained in the crystalline state by heating the double chloride of uranium and sodium in a current of hydrogen containing the vapour of selenium (Colani, Compt. rend. 1903, 137, 382; Ann. Chim. Phys. 1907, [viii.] 12, 59).

Uranyl selenide is produced by heating uranosouranic oxide with selenium and potassium cyanide (Milbauer, Zeitsch. anorg. Chem. 1904, 42, 450).

Uranium telluride U_2Te_3 is prepared by fusing the double chloride of sodium and uranium with sodium telluride in an atmosphere of hydrogen (Colani, *l.c.*).

Uranium nitride U_3N_4 is a stable, greyish-black powder, prepared by heating uranous chloride in ammonia, and igniting the product mixed with ammonium chloride, once more in a stream of ammonia (Kohlschütter, Annalen, 1901, 317, 158). Uranium unites directly with nitrogen at 1000°, a yellow nitride being produced, the composition of which is not known (Moissan, Compt. rend. 1896, 122, 274).

Uranium phosphide U_3P_4 is obtained by fusing sodium uranous chloride with aluminium phosphide in a stream of hydrogen (Colani, *l.c.*) The *arsenide* U_3As_4 and *antimonide* U_3Sb_4 are similarly prepared. All three compounds are obtained as black crystalline powders; they are easily oxidised by nitric acid.

Uranium carbide U_2C_3 is prepared by strongly heating a mixture of 500 parts of uranosouranic oxide and 60 parts of carbon in the electric furnace. It is a lustrous, crystalline solid of sp.gr. 11·28 at 18°, and is harder than quartz, although not so hard as corundum. It is decomposed by fluorine when gently warmed; chlorine readily attacks it at 350°, whilst it reacts with oxygen at 370°. Uranium carbide is decomposed by water, a very complex change occurring. About one-third of the carbon is evolved in combination with hydrogen, mainly as methane, but mixed with a little ethylene and traces of acetylene; the gaseous mixture contains about 15 p.c. of free hydrogen. The remainder of the carbon is converted into a mixture of solid and liquid hydrocarbons (Moissan, Compt. rend. 1896, 122, 274). A shower of brilliant sparks is produced when two pieces of the carbide are rubbed together.

Uranium silicide USi_2 is obtained from a mixture of silica and uranosouranic oxide by the aluminothermic process (*v.* THERMIT PROCESS). It crystallises in the cubic system, and has a density of 8·0. At 500° it reacts with chlorine giving a mixture of uranous and silicon chlorides (Defacqz, *ibid.* 1908, 147, 1050).

SALTS OF URANIUM.

Uranyl acetate $UO_2(C_2H_3O_2)_2,2H_2O$ is prepared by dissolving in warm acetic acid the yellowish-red mass produced by heating uranyl nitrate until evolution of oxygen commences. It crystallises in yellow, monoclinic needles, and is used in photography and also for the volumetric estimation of phosphates.

Uranous arsenate $UH_2(AsO_4)_2,2H_2O$ (Aloy, Bull. Soc. chim. 1899, [iii.] 21, 613; Rammelsberg, Pogg. Ann. 1842, 55, 318; 56, 125).

Uranyl arsenate $UO_2{\cdot}H(AsO_4)_2,4H_2O$, a yellow powder, insoluble in water and acetic acid, is obtained by double decomposition (Werther, Annalen, 1848, 68, 313). Several arsenates occur as minerals, *e.g.* *trögerite* $(UO_2)_3(AsO_4)_2,12H_2O$; *walpurgite*, a basic bismuth uranyl arsenate; and *uranospinite*, a calcium uranium arsenate.

Uranyl bromate $UO_2(BrO_3)_2,xH_2O$, *v.* Rammelsberg, Pogg. Ann. 1842, 55, 77.

Uranous carbonate and **uranyl carbonate** are not known (Parkman, Amer. J. Sci. 1862, [ii.] 34, 326). Numerous double carbonates exist. *Potassium uranyl carbonate* $UO_2(CO_3),2K_2CO_3$ is obtained by dissolving potassium uranate in potassium bicarbonate and evaporating the solution at a moderate temperature; the corresponding ammonium and sodium salts are prepared in a similar manner (Ebelmen, Ann. Chim. Phys. 1842, [iii.] 5, 189; Anthon, J. 1860, 698; de Coninck, Bull. Acad. roy. Belg. 1904, 363, 448). They form yellow, rhombic prisms, which are not very soluble in water, but much more soluble in alkali carbonate solutions. The ammonium salt loses ammonia on keeping. Another ammonium compound $2UO_2{\cdot}CO_3{\cdot}3(NH_4)_2CO_3,4H_2O$ has been obtained by mixing uranyl nitrate and ammonium carbonate (Giolitti and Vecchiarelli, Gazz. chim. ital. 1905, 35, ii. 170). *Uranyl calcium carbonate* $UO_2CO_3{\cdot}CaCO_3,10H_2O$ occurs as the mineral *liebigite* in apple-green warty masses.

Uranyl chlorate $UO_2(ClO_3)_2,xH_2O$ is a very soluble substance, which readily decomposes when heated (Rammelsberg, *l.c.*).

Uranyl chromate $UO_2{\cdot}CrO_4$ is obtained by adding uranic oxide to boiling chromic acid solution; it crystallises, on cooling the solution, in yellow needles, containing $5\frac{1}{2}H_2O$ (Formánek, Annalen, 1890, 257, 108), or $3H_2O$ (Orloff, Chem. Zeit. 1907, 31, 375). The double salt

$$K_2CrO_4{\cdot}2UO_2{\cdot}CrO_4,6H_2O$$

is obtained as yellow monoclinic crystals by treating potassium uranate with chromic acid. The ammonium salt is isomorphous with the preceding salt; the sodium salt contains $10H_2O$ (Formánek, *l.c.*).

Uranyl iodate $UO_2(IO_3)_2$ is precipitated on mixing boiling solutions of uranyl nitrate and sodium iodate in dilute nitric acid; it forms yellow prisms, slightly soluble in water. A hydrate $UO_2(IO_3)_2,5H_2O$ is also known (Ditte, Thèse de doctorat ès Sc. Paris, 1870).

Uranous nitrate has not yet been prepared in the solid form (Isambert, Compt. rend. 1875, 80, 1087).

Uranyl nitrate $UO_2(NO_3)_2$. The anhydrous salt is not known, but numerous hydrates have been prepared. The trihydrate $UO_2(NO_3)_2,3H_2O$ crystallises in yellow, monoclinic forms, and melts at 121·5°; the dihydrate is rhombic and melts at 179·3° (Vasilieff, J. Russ. Phys. Chem. Soc. 1910, 42, 570). The commercial salt is the hexahydrate $UO_2(NO_3)_2,6H_2O$. It is formed when any of the oxides of uranium are dissolved in nitric acid, and is prepared commercially by heating ammonium uranate and dissolving the residue in nitric acid (Janda, Oester. Zeit. Berg-Hütt. 1901, 49, 325). For methods of preparation from pitchblende, *v.* Péligot, Ann. Chim. Phys. 1844, [iii.] 12, 557; Ebelmen, *ibid.* 1842, [iii.] 5, 186. The hexahydrate forms lemon-yellow, fluorescent, rhombic prisms, which melt at 60·2° and deliquesce in the air (Vasilieff, *l.c.*; de Coninck, Compt. rend. 1900, 131, 1219, 1303; 1901, 133, 90, 204; Bull. Acad. roy. Belg. 1901, 222; 1909, 743). Water at 18° dissolves twice its weight of the salt. It is very soluble in alcohol and ether, and is best purified by crystallisation from the latter solvent. The aqueous solution is slightly hydrolysed, and has an acid reaction (Ley, Zeitsch. physikal. Chem. 1899, 30, 193; Ber. 1900, 33, 2658; Dittrich, Zeitsch. physikal. Chem. 1899, 29, 449).

Double nitrates of the type $RUO_2(NO_3)_3$, where R may be potassium, ammonium, thallium, rubidium, or cæsium, but not sodium or lithium, are obtained by crystallising solutions of the mixed salts in nitric acid. Water decomposes them into their components (Meyer and Wendel, Ber. 1903, 36, 4055; Rimbach, *ibid.* 1904, 37, 461).

Uranyl nitrate is used in photography, and also for the volumetric estimation of phosphates and arsenates.

Uranous phosphate $UH_2(PO_4)_2,5H_2O$ (Aloy, Bull. Soc. chim. 1899, [iii.] 21, 613).

Uranyl phosphate $UO_2{\cdot}HPO_4$. This is precipitated in an amorphous form by adding a soluble phosphate to uranyl nitrate solution. When this precipitate is continuously boiled with dilute hydrochloric acid for a long time, it is converted into $UO_2{\cdot}HPO_4,4H_2O$, which crystallises in tetragonal plates (Bourgeois, *ibid.*

1897, [iii.] 19, 733). The *dihydrogen phosphate* $UO_2(H_2PO_4)_2,3H_2O$ is obtained by heating uranic oxide with dilute phosphoric acid, and concentrating the solution. It separates in small yellow crystals (Werther, J. pr. Chem. 1848, [i.] 43, 321). *Uranyl ammonium phosphate* $UO_2(NH_4)PO_4.xH_2O$ is a greenish-yellow precipitate formed by the addition of a soluble phosphate to a mixture of a uranyl and an ammonium salt. It is obtained in the volumetric estimation of phosphates. The precipitate is insoluble in acetic acid. Upon ignition it leaves a yellow residue of *uranyl pyrophosphate* $(UO_2)_2P_2O_7$.

Various phosphates occur in nature, *e.g.* *chalcolite* or *torberite* $(Cu(UO_2)_2(PO_4)_2.10H_2O)$ and *autonite* or *uranite* $(Ca(UO_2)_2(PO_4)_2.8H_2O)$.

Uranous sulphate $U(SO_4)_2.8H_2O$ is prepared by dissolving the green oxide in dilute sulphuric acid, adding alcohol and allowing the solution to crystallise. The mother liquor contains uranyl sulphate; on exposure to light it is reduced to uranous sulphate, and another crop of crystals is obtained. A large number of other hydrates are known, *e.g.* di-, tri-, tetra-, penta-, hexa-, hepta-, and nonohydrates (Orloff, J. Russ. Phys. Chem. Soc. 1902, 34, 381; de Coninck, Bull. Acad. roy. Belg. 1901, 483; Kohlschütter, Ber. 1901, 34, 3628; Giolitti and Bucci, Gazz. chim. ital. 1905, 35, ii. 151, 162; Giolitti and Liberi, *ibid.* 1906, 36, ii. 443). The tetrahydrate is a stable substance, and the nonohydrate $U(SO_4)_2,9H_2O$ crystallises from aqueous solution in green monoclinic prisms that frequently exhibit twinning and are isomorphous with thorium sulphate

$$Th(SO_4)_2,9H_2O$$

(Rammelsberg, Zeitsch. Krystall. 1889, 15, 640). Uranous sulphate forms double salts with sulphates of the alkali metals, *e.g.*

$$U(SO_4)_2\cdot K_2SO_4,2H_2O$$

(Kohlschütter, Ber. 1901, 34, 3619). Aqueous solutions of uranous sulphate are readily hydrolysed, basic sulphates being precipitated.

A sulphate of the composition $UH(SO_4)_3$, which is supposed to contain trivalent uranium, has been described (Rosenheim and Loebel, Zeitsch. anorg. Chem. 1908, 57, 234).

Uranyl sulphate $UO_2\cdot SO_4$ is obtained by dissolving the hydroxide of uranium trioxide in concentrated sulphuric acid and crystallising the solution (Schultz-Sellack, Ber. 1871, 4, 13); or by drying either of its hydrates at 300°. It forms yellow fluorescent crystals. The hydrate $UO_2\cdot SO_4,3\frac{1}{2}H_2O$ is obtained by concentrating a solution of uranic hydroxide in dilute sulphuric acid; the solution does not crystallise readily. Another method is to dissolve uranosouranic oxide in concentrated sulphuric acid, dilute, and boil with nitric acid to oxidise the uranous sulphate present. The hydrate forms citron yellow prisms, which effloresce in air, losing water and leaving the trihydrate $UO_2\cdot SO_4.3H_2O$. This dissolves in twenty times its weight of water at ordinary temperatures (de Coninck, Bull. Acad. roy. Belg. 1901, 222, 349; 1902, 94, 161). Dried *in vacuô* or at 100° it retains 1 molecule of water. When dissolved in moderately concentrated sulphuric acid, a beautiful yellow, fluorescent, crystalline acid sulphate

$$UO_2\cdot SO_4\cdot H_2SO_4$$

crystallises out. The pyrosulphate $(UO_2)_2S_2O_7$ crystallises from a solution of the anhydrous sulphate in pyrosulphuric acid (Schultz-Sellack, Ber. 1871, 4, 13).

Uranyl sulphate forms a double sulphate with hydroxylamine sulphate (Rimbach, Ber. 1904, 37, 461); a salt $Tl_2SO_4\cdot UO_2SO_4,3H_2O$ with thallous sulphate (Kohn, Zeitsch. anorg. Chem. 1908, 59, 111); and combines with equimolecular quantities of the sulphates of ammonium, potassium, lithium, cæsium, and magnesium, forming double salts which crystallise with from 2 to 5 molecules of water (de Coninck, Bull. Acad. roy. Belg. 1904, 1171; 1905, 50, 94, 151, 182; de Coninck and Chauvenet, *ibid.* 1908, 50).

A number of *basic sulphates* occur naturally, *e.g.* *zippéite* $(UO_2\cdot SO_4\cdot UO_2)$ and *uraconite* $(UO_2\cdot SO_4\cdot 2UO_3,14H_2O)$, which are alteration-products of pitchblende.

Uranyl sulphite. The crystalline precipitate obtained by evaporating a solution of uranic oxide in aqueous sulphurous acid, or by passing sulphur dioxide into an aqueous solution of uranyl acetate, has the empirical composition $UO_2\cdot SO_2,4H_2O$ (Girard, Compt. rend. 1852, 34, 22). According to Kohlschütter (Annalen, 1901, 314, 311) it is really uranyl sulphurous acid $SO_2H\cdot UO_2\cdot OH,3H_2O$ (*cf.* Ley, Ber. 1900, 33, 2659).

Tungstates, *v.* Rammelsberg, Pogg. Ann. 1843, 59, 31; Lefort, Compt. rend. 1878, 87, 748.

Detection and estimation. In qualitative analysis uranium is obtained together with iron. All the uranyl salts of weak acids, *e.g.* carbonate, sulphide, phosphate, &c., are soluble in ammonium carbonate and the other alkali carbonates. The ferrocyanide, a brown precipitate, insoluble in dilute acids, is characteristic; alkalis turn it yellow. Uranium is usually weighed as uranosouranic oxide, or else as uranyl pyrophosphate; uranous salts may be titrated with permanganate. *V.* ANALYSIS, and Finn, J. Amer. Chem. Soc. 1906, 28, 1443; McCoy and Bunzel, *ibid.* 1909, 31, 367; Giolitti, Gazz. chim. ital. 1904, 34, ii. 166; Mazzucchelli, Atti. R. Accad. Lincei. 1906, [v.] 15, ii. 429, 494; Campbell and Griffin, J. Ind. Engin. Chem. 1909, 1, 661; Ibbotson and Clark, Chem. News. 1911, 103, 146.

URANIUM MICA *v.* AUTUNITE; TORBERNITE; URANITE.

URANIUM X. Estimated at.wt. 230·5. A radioactive element produced by the disintegration of uranium. It emits two kinds of β- rays, and also γ- rays, and its presence in ordinary uranium salts is responsible for the penetrative rays they emit. Uranium salts, when freed from uranium X, only emit α-rays.

Uranium X may be separated in a number of ways. When a concentrated solution of uranyl nitrate (sp.gr. of solution 2·05) is allowed to cool, the mother liquor left after removing the crystals formed contains about 85 p.c. of the uranium X present (Soddy and Russell, Phil. Mag. 1909, [vi.] 18, 620). If crystals of hydrated uranyl nitrate are shaken with ether, two layers are formed; the aqueous (lower) layer retains the uranium X. In the purification of a uranyl solution from iron, aluminium, &c., by pouring into excess of ammonium carbonate, the precipitated impurities contain all the uranium X.

If this precipitate is dissolved in concentrated hydrochloric acid, and the solution extracted with ether, saturated with hydrogen chloride, the ferric chloride is removed, but not the uranium X, which remains in the aqueous layer (Lloyd, J. Phys. Chem. 1910, 14, 509; Soddy, Phil. Mag. 1909, [vi.] 18, 861). It has been recommended to add a thorium salt to a uranyl salt, and then precipitate the thorium in acid solution as fluoride; the precipitate contains the uranium X (Keetman, Jahr. Radioaktivitat, 1909, 6, 269; Ritzel, Zeitsch. physikal. Chem. 1909, 67, 725). By using a lanthanum salt containing a very little thorium, converting the precipitated fluorides into sulphates and then precipitating by boiling with sodium thiosulphate, a precipitate is obtained, consisting mainly of sulphur, which on ignition leaves a very slight residue containing all the uranium X originally present (*cf.* Antonoff, Phil. Mag. 1911, [vi.] 22, 431).

Chemically, uranium X seems to resemble thorium very closely; for its radioactive properties, *v.* RADIOACTIVITY.

URANIUM YELLOW *v.* URANIUM.

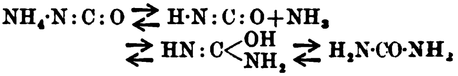
URAO. A native form of sodium sesquicarbonate $Na_4H_2(CO_3)_3,2H_2O$, found in South America, Africa and other places.

URARI *v.* CURARA.

p-**URAZINE** *v.* HYDRAZINES.

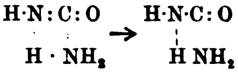
UREA, *carbamide*, $CO{<}\genfrac{}{}{0pt}{}{NH_2}{NH_2}$ occurs in human urine to the extent of 1·5 p.c. to 2 p.c.; in the urine of other mammalia, especially the carnivora; in small quantities in the blood, bile, milk, perspiration, the aqueous humour of the eye, and other animal fluids (Würtz, Compt. rend. 1859, 49, 52; Popp, Annalen, 1869, 151, 88; Argutinsky, Pflüger's Archiv. 1891, 46, 594; North, Proc. Roy. Soc. 1886, 39, 443; Pautz, Zeitsch. biol. 1894, 31, 212); in the liver, muscle and blood of the dog-fish, the blood containing 2·78 p.c. (v. Shroeder, Zeitsch. physiol. Chem. 1890, 14, 576; Baglioni, Beitr. chem. Physiol. Path. 1906, 9, 50); in the bile and blood of other fish (Hammarsten, Zeitsch. physiol. Chem. 1898, 24, 322; Baglioni, *l.c.*). In the vegetable kingdom urea has been found in *Lycoperdon bovista*, *Psolliota campestris* and other higher fungi to the extent of 4·3 p.c. of the dry weight, and is present in minute quantities in the juice from the washed leaves of a number of plants and also in seedlings of wheat, barley, maize, peas, clover, and beans (Bamberger and Landseidl, Monatsh. 1903, 24, 218; Gaze, Arch. Pharm. 1905, 243, 78; Goris and Mascré, Compt. rend. 1908, 147, 1488; Fosse, *ibid.* 1912, 155, 851; 1913, 156, 567).

Urea was first obtained synthetically by Wöhler in 1828 from ammonium cyanate, which undergoes a spontaneous transformation into its isomeride urea when an aqueous solution is evaporated at the temperature of boiling water. The mechanism of the reaction has been exhaustively studied by Walker and others (Chem. Soc. Trans. 1895, 67, 746; 1896, 79, 193; 1897, 71, 489; 1900, 77, 30), who have shown: (1) that the reaction is a reversible one, equilibrium being reached in a decinormal solution when ere is about 95 p.c. of urea and 5 p.c. of am-ium cyanate present; (2) that the reaction bimolecular one; (3) that the velocity of the reaction is thirty times as great in 90 p.c. ethyl alcoholic as in aqueous solutions; and (4) that pure dry ammonium cyanate passes rapidly into urea when heated at about 80°. These authors suggest that the active molecules in the reaction are ammonium ions and cyanic acid ions, $NH_4^{\cdot}+CNO'=CO(NH_2)_2$; and that the increased velocity of the reaction in alcoholic solution is due to the effect of the alcohol in increasing the rate at which the dissociated ions interact, and this more than counterbalances the diminution in the velocity due to the diminished degree of electrolytic dissociation of the cyanate. Another explanation of the reaction offered by Chattaway (Chem. Soc. Trans. 1912, 101, 170) is that ammonium cyanate dissociates into ammonia and cyanic acid, that these interact to form *iso*urea, which rapidly undergoes molecular rearrangement



$$NH_4{\cdot}N{:}C{:}O \rightleftarrows H{\cdot}N{:}C{:}O+NH_3 \rightleftarrows HN{:}C{<}\genfrac{}{}{0pt}{}{OH}{NH_2} \rightleftarrows H_2N{\cdot}CO{\cdot}NH_2$$

Wheeler and others (J. Amer. Chem. Soc. 1912, 34, 1269) offer a somewhat simpler explanation of the interaction between the cyanic acid and ammonia by introducing the idea of partial valency



$$\begin{matrix} H{\cdot}N{:}C{:}O \\ \vdots \quad \vdots \\ H \cdot NH_2 \end{matrix} \rightarrow \begin{matrix} H{\cdot}N{\cdot}C{:}O \\ \vdots \\ H\,NH_2 \end{matrix}$$

Urea can be obtained from lead cyanate by direct hydrolysis with boiling water (Cumming, Chem. Soc. Trans. 1903, 83, 1391); by heating ammonium sesquicarbonate or ammonium carbamate at 130°–135° under pressure (Bourgeois, Bull. Soc. chim. 1897, [iii.] 17, 474; Fichter and Becker, Ber. 1911, 44, 3473); by passing a mixture of ammonia and carbon dioxide through a red hot tube (Mixter, Amer. Chem. J. 1882, 4, 35); by the action of carbonyl chloride on ammonia (Hofmann, Quart. J. Chem. Soc. 1850, 2. 44); by passing a stream of air charged with ammonia and benzene vapour or acetylene over a heated platinum spiral (Herroun, Chem. Soc. Trans. 1881, 39, 471); by heating a solution of carbon monoxide in ammonium cuprous chloride at 105° under pressure (Jouve, Compt. rend. 1899, 128, 114); by the decomposition of copper or ammonium fulminate with sulphuretted hydrogen (Gladstone, Quart. J. Chem. Soc. 1849, 1, 228); by the decomposition of an aqueous solution of prussic acid (Campani, Gazz. chim. ital. 1871, 1, 472), or by the oxidation of potassium cyanide with potassium permanganate or sodium hypochlorite (Volhard, Annalen, 1890, 259, 377; Reychler, Bull. Soc. chim. 1893, [iii.] 9, 427). Urea is also obtained by the hydrolysis of guanidine (Flemming, Chem. Zeit. 1900, 24, 56), arginine (Schulze and Likiernik, Ber. 1891, 24, 2701) or lysatine (Drechsel, *ibid.* 1890, 23, 3096) with barium hydroxide solution: and is a constant product of oxidation with acid potassium permanganate of a large number of organic compounds containing nitrogen: for example, acid amides and amino acids (Hofmeister, Chem. Zentr. 1896, ii. 389; Jolles, Ber. 1900, 33, 2834; J. pr. Chem. 1901, [ii.] 63, 516), and proteins (Ritter, Compt. rend. 1872, 73, 1219; Hofmeister, *l.c.*; Hugounenq, Compt. rend. 1901, 132, 1240; Jolles, Ber. 1901, 34, 1447; Fosse, Compt. rend. 1912, 154, 1187, 1819).

Urea is usually obtained from urine by treating the concentrated filtered liquid with a hot saturated solution of oxalic acid and decomposing the sparingly soluble urea oxalate thus obtained with powdered chalk; the filtrate is decolorised with animal charcoal and evaporated until the urea crystallises out on cooling. Another method consists in extracting the urea with alcohol from the syrup obtained by evaporating the urine, precipitating the urea as the sparingly soluble nitrate by the addition of concentrated nitric acid, and decomposing the salt by boiling with barium carbonate and alcohol; the urea is obtained by crystallisation from the filtrate.

Carbamide can be prepared on a large scale by passing dry ammonia into fused phenyl carbonate until the odour of ammonia is persistent. The product is poured into hot water, when it separates into two layers consisting respectively of phenol and a solution of carbamide; 5 kilos. of phenyl carbonate yield 1 kilo. of carbamide and the whole of the phenol is recovered. The phenyl carbonate is obtained in an almost theoretical yield by passing dry carbonyl chloride into a solution of phenol in its equivalent quantity of dilute caustic soda (Hentschel, Ber. 1884, 17, 1286). By a similar reaction, guaiacol carbonate is rapidly converted into carbamide and guaiacol when an alcoholic solution is saturated with ammonia (Cazeneuve, Compt. rend. 1896, 122, 999).

Urea crystallises in needles, or in four-sided rhombic anhydrous prisms; it is readily soluble in water, 1 grm. of water dissolving 0·779 grm. of urea at 5·5°, 1·00 grm. at 17·1° and 1·094 grm. at 20·92° (Krummacher, Zeitsch. biol. 1905, 46, 302). It dissolves in five parts of cold alcohol, is soluble in methyl and in amyl alcohol, and is insoluble in ether, ethyl acetate or chloroform. The heat of combustion is 2·532 cal., and the heat of solution 3·57 cal. (Krummacher, *l.c.*).

Urea melts at 130°–132°, and sublimes readily when heated under reduced pressure at 120°–130° (Bourgeois, Bull. Soc. chim. 1892, [iii.] 7, 45). Urea decomposes when heated above its melting-point; at 150°–160° it loses ammonia forming *biuret* $NH_2\cdot CO\cdot NH\cdot CO\cdot NH_2$, which on further heating decomposes into ammonia, ammonium cyanate, melanuric acid.

$$C_3N_3(OH)_2NH_2$$

and cyanuric acid $C_3N_3(OH)_3$ (Drechsel, J. pr. Chem. 1874, [ii.] 9, 284). When urea is sublimed in a vacuum at 160°–190°, the sublimate consists of ammonium cyanate (Escales, Chem. Zeit. 1911, 35, 595). When an aqueous solution of urea is boiled, it is partially converted into ammonium cyanate. The reaction is a reversible one, equilibrium being reached in a N/10 solution, when there is about 5 p.c. ammonium cyanate present (Walker and Hambly, Chem. Soc. Trans. 1895, 67, 746; Fawsitt, Zeitsch. physikal. Chem. 1902, 41, 602). When heated with water in a sealed tube at 180°, urea undergoes complete hydrolysis, forming ammonium carbonate. Urea is decomposed by the action of nitrous acid, yielding nitrogen and carbon dioxide (Claus, Ber. 1871, 4, 140). It is oxidised by a hot acid solution of potassium permanganate, yielding two vols. CO_2 and 1 vol. N (Wanklyn and Gamgee, Chem. Soc. Trans. 1868, 21, 25). By the action of sodium hypochlorite or hypobromite, urea is converted into carbon dioxide, nitrogen and water. For an explanation of the course of this reaction, compare Schestakow (J. Russ. Phys. Chem. Soc. 1905, 37, 1), Dehn (J. Amer. Chem. Soc. 1910, 31, 1220). Urea is decomposed by bromine, yielding cyanuric acid, ammonium bromide and nitrogen: chlorine has a similar reaction on fused urea (Smolka, Monatsh. 1887, 8, 64). Urea is converted into cyanamide $NC\cdot NH_2$ by the action of sodium (Fenton, Chem. Soc. Trans. 1882, 41, 262) or of sulphuryl chloride (Moureu, Bull. Soc. chim. 1894, [iii.] 11, 1068).

Urea readily undergoes bacterial fermentation with production of ammonium carbonate (Miguel, Compt. rend. 1890, 111, 397; Frankland, Chem. Soc. Trans. 1885, 47, 175; Hatton, *ibid.* 1881, 39, 256); a ferment present in urine is particularly active in causing this decomposition, and if this ferment is collected on paper by filtration, washed and dried at 35°–40°, its activity revives when brought into contact with water; and such papers, when previously coloured with turmeric, form a convenient test for urea, becoming deep brown when dipped into a solution containing even $\frac{1}{10000}$ part of urea (Musculus, Compt. rend. 1874, 78, 132).

Detection. Urea can be detected by the formation of its sparingly soluble nitrate or oxalate. In the case of the latter salt, the precipitation is facilitated by using an amyl alcoholic solution of the urea and of the oxalic acid (Brücke, Monatsh. 1881, 3, 195). The *biuret* test is the commonest test for urea. It consists in heating gently the urea until it ceases to evolve ammonia freely, dissolving the residue in a little water and adding a few drops of very dilute copper sulphate solution, on the subsequent addition of a drop of concentrated potassium hydroxide, a beautiful violet colour is developed. If the urea is in solution, it may be detected by evaporating to dryness with hydrochloric acid, heating the residue until it ceases to evolve thick white fumes and then dissolving in ammonia; on adding barium chloride solution and stirring, crystals of barium cyanurate separate on the lines of friction made by the rod; or copper sulphate may be added to the ammoniacal solution of the residue, when violet crystals of cuprammonium cyanurate separate out (Bloxam, Chem. News, 1883, 47, 285). Other colour reactions that can be used for the detection of urea are (1) the formation of a fine purple violet colour, when a solution of urea is treated with a concentrated solution of furfurol and a few drops of concentrated hydrochloric acid (Schiff, Ber. 1877, 10, 773); (2) the development of an intense blue colour when minute quantities of urea (or other compounds containing the $\cdot NH\cdot CO\cdot NH_2$ group) and methylfuril ($C_4H_3O\cdot CO\cdot CO\cdot C_4H_2O\cdot CH_3$) are mixed on a filter paper and treated with a drop of fuming hydrochloric acid (Fenton, Chem. Soc. Trans. 1903, 83, 187; Proc. Camb. Phil. Soc. 1911, 16, 64); (3) the development of the characteristic red colour of the sodium violurate when the urea (or its mono- or sym. di-substituted derivatives) is condensed with malonic acid by cautiously heating the mixture moistened with phosphoryl chloride, the resulting barbituric acid dissolved in water, neutralised with solid sodium carbonate, and then treated with a crystal of sodium nitrite and a drop of acetic acid (Whiteley, *private communication*); (4) urea condenses with *o*-nitrobenzaldehyde when heated in alcoholic solution. The *o*-nitrobenzodiureide

$$NO_2{\cdot}C_6H_4{\cdot}CH(NH{\cdot}CO{\cdot}NH_2)_2$$

thus obtained melts at 200°, and if present in very small amount may be readily detected by decomposing it with dilute hydrochloric acid and testing for *o*-nitrobenzaldehyde by the red colour it gives with phenylhydrazine (Lüdy, Monatsh. 1889, 10, 295).

Estimation. The determination of the amount of urea present in urine, blood serum or other animal liquids, is a problem of great physiological importance. Of the large number of methods that have been described for the estimation of urea, only those are now in use that involve the conversion of urea into ammonia, under such conditions that other nitrogenous substances that may be present in the specimen are not simultaneously hydrolysed. The most important methods are those of Folin and of Benedict, Mörner and Sjöquist and of Pflüger and Bleibtreu.

I. Folin's method is based on the fact that urea is quantitatively converted into ammonia and carbon dioxide when heated with fused magnesium chloride $MgCl_2,6H_2O$. In using this method for the estimation of urea in urine, 3 c.c. of the sample are boiled for half an hour with 20 grms. of hydrated magnesium chloride and 2 c.c. concentrated hydrochloric acid in a small reflux apparatus supplied with a special 3-bulb safety tube. After careful dilution, 7 c.c. of 20 p.c. sodium hydroxide are added to liberate magnesium hydroxide and the ammonia distilled over into a known volume of N/10 acid, the distillation being prolonged until the contents of the flask are almost dry. Allowance must be made for the ammonia present in the magnesium chloride (Folin, Zeitsch. physiol. Chem. 1901, 32, 504; 1902, 36, 333). In this method, creatinine yields traces of ammonia and allantoin yields all its nitrogen as ammonia. Benedict (J. Biol. Chem. 1910, 8, 405) modifies the method by adding to the urine potassium hydrogen sulphate, zinc sulphate, a little powdered pumice, and a piece of paraffin to prevent frothing; the mixture is boiled to dryness, the residue heated at 162°–165° for an hour, then mixed with sodium hydroxide and the liberated ammonia distilled into standard acid.

II. In the Mörner-Sjöquist method of estimating urea in urine, uric acid, purine bases, tyrosine, allantoin, &c., are removed by precipitation with barium chloride and hydroxide in a mixture of alcohol and ether. The filtrate and washings are evaporated at 55° to about 25 c.c., a little water and magnesia added and the distillation continued until the steam has no longer an alkaline reaction. The volume is then concentrated to 10–15 c.c. and the nitrogen present estimated by the Kjeldahl method (Chem. Soc. Abstr. 1891, 758; compare Braunstein, Zeitsch. physiol. Chem. 1900, 31, 381).

III. In the Pflüger-Bleibtreu method for the estimation of urea in urine, the nitrogenous compounds other than urea are precipitated by means of a mixture of hydrochloric and phosphotungstic acids; the urea decomposed in the neutralised filtrate by heating it with phosphoric acid, and the ammonia estimated. For working details of this and the other methods, see Abderhalden's Handbuch der Biochemisches Arbeitsmethoden, vol. iii. part 2, 776–782.

Derivatives. *Salts.* Urea forms salts with metals; *silver urea* $CO(NHAg)_2$ (Mulder, Ber. 1873, 6, 1019); *monopotassium urea* CON_2H_3K, colourless needles; *dipotassium urea* $CON_2H_2K_2$, gelatinous mass (Franklin and Stafford, Amer. Chem. J. 1902, 28, 83). It also forms salts with acids, some of which combine with metallic salts to form stable crystalline double salts. The *nitrate* $CO(NH_2)_2{\cdot}HNO_3$ forms sparingly soluble monoclinic crystals that decompose at 140° (Gaubert, Compt. rend. 1907, 145, 378); the *hydrochloride* $CO(NH_2)_2{\cdot}HCl$ dissociates in aqueous solution (Datta, Chem. Soc. Trans. 1912, 101, 166); the *phosphate* $CO(NH_2)_2{\cdot}H_3PO_4$, large rhombic crystals, readily soluble in alcohol or water; *acetate* $CO(NH_2)_2,C_2H_4O_2,2H_2O$ large deliquescent crystals (Matignon, Compt. rend. 1891, 112, 1367); *glycine urea*

$$CO(NH_2)_2{\cdot}NH_2{\cdot}CH_2{\cdot}CO_2H,$$

large crystals (Matignon, Bull. Soc. chim. 1894, [iii.] 11, 575); the *salicylate* (*ursal*)

$$CO(NH_2)_2{\cdot}C_7H_6O_3$$

has m.p. 122°; the *acid* salt $CO(NH_2)_2{\cdot}2C_7H_6O_3$ has m.p. 115°; the *quinate* (*urol, urocol*)

$$[CO(NH_2)]_2C_7H_{12}O_6$$

m.p. 107°; the *picrate* $CO(NH_2)_2{\cdot}C_6H_3O_7N_3$ decomposes at 142° (Smolka, Monatsh. 1885, 6, 915); the *oxalate* $[CO(NH_2)_2]_2C_2H_2O_4$ forms rhombic plates or prisms, sparingly soluble in water (1 : 23), less so in alcohol (1 : 62), amyl alcohol, and insoluble in ether. With hydrogen peroxide urea forms the *compound*

$$CO(NH_2)_2{\cdot}H_2O_2$$

crystallising in large transparent crystals (Tanatar, J. Russ. Phys. Chem. Soc. 1908, 40, 376). Urea forms crystalline *compounds* with *sodium chloride* $CO(NH_2)_2{\cdot}NaCl,H_2O$ rhombic plates or prisms, m.p. 60°–70°; with *ammonium chloride* $CO(NH_2)_2{\cdot}NH_4Cl$ quadratic plates or needles that readily dissociate; with *calcium bromide* (*ureabromin*) $4CO(NH_2)_2{\cdot}CaBr_2$, m.p. 186°, which has therapeutic properties resembling those of the alkali bromides (Biltz, Pharm. Zentr. 1912, 53, 245); with *mercuric chloride*

$$CO(NH_2)_2{\cdot}HgCl_2;$$

with *zinc chloride* $CO(NH_2)_2{\cdot}ZnCl_2$; with *cadmium chloride* $CO(NH_2)_2,CdCl_2$; with *silver nitrate* $CO(NH_2)_2,AgNO_3$; with *palladium chloride* $PdCl_2{\cdot}2CO(NH_2)_2$; and with *magnesium bromide* $MgBr_2{\cdot}6CO(NH_2)_2$, m.p. 167°–170°, with decomposition, and $MgBr_2{\cdot}4CO(NH_2)_2$ decomposes at 165°–170° (Menschutkin, Petersberger polytechn. Inst., 1906, 6, 101). Among the double salts formed by urea are the *platinichlorides* $[CO(NH_2)_2{\cdot}HCl]_2{\cdot}PtCl_4,2H_2O$, hygroscopic yellow prisms (Heintz, Annalen, 1879, 198, 91) and $[CO(NH_2)_2]_4{\cdot}H_2PtCl_6$, m.p. 119°–120°, red prismatic crystals (Pickard and Kenyon, Chem. Soc. Trans. 1907, 91, 902); the *aurichlorides* $2CO(NH_2)_2{\cdot}HCl{\cdot}AuCl_3$ and $CO(NH_2)_2{\cdot}HCl{\cdot}AuCl_3,H_2O$; the *quinine hydrochloride* $C_{20}H_{24}N_2O_2{\cdot}HCl,CO(NH_2)_2{\cdot}HCl,5H_2O$, nd similar compounds containing quinidine nd cinchonidine (Drygin, Chem. Zentr. 1881, 45). The compounds with *mercuric nitrate* $CO(NH_2)_2\cdot Hg(NO_3)_2\cdot 3HgO$,

$$2CO(NH_2)_2\cdot Hg(NO_3)_2\cdot 2HgO$$

nd $2CO(NH_2)_2\cdot Hg(NO_3)_2\cdot HgO$ are obtained by recipitation between urea and mercuric nitrate nder different conditions of concentration. Jrea also combines with mercuric salts to form alts of the divalent radicle $CO(NHHg)_2$, mercurocarbamide'; the *hydroxide*

$$CO(NH\cdot HgOH)_2\ ;$$

he *chloride* $CO(NH\cdot HgCl)_2$, and

$$CO(NH\cdot HgCl)_2\cdot CO(NH_2)_2\cdot 2HCl\ ;$$

he *nitrate* $CO(NH\cdot HgNO_3)_2$, *sulphate*

$$CO(NHHg)_2SO_4,$$

nd the *acetate* $CO(NH\cdot HgOAc)$ (Ruspaggiari, lazz. chim. ital. 1897, 27, I, 1). Salts containg chromium complexes and urea have been lescribed by Sell (Proc. Roy. Soc. 1883, 33, 67; 1889, 45, 321).

Acyl derivatives of urea, v. UREIDES.

Chloro and *nitro derivatives. Chlorocarbamide*

$$NH_2\cdot CO\cdot NHCl$$

lecomposes at 71°, dissolves in five parts of rater at ordinary temperature, giving a neutral olution that loses nitrogen and forms biuret. t reacts slowly in aqueous solution on aliphatic etones, yielding the monochloroketone (Béhal nd Detoeuf, Compt. rend. 1911, 153, 681, 1229). *Dichlorocarbamide* $CO(NHCl)_2$, prepared by passng a rapid stream of chlorine into a well-cooled olution of urea in water, forms colourless lates that melt with decomposition at 82° when autiously heated and detonate when rapidly eated, forming nitrogen chloride; on decomosition with ammonia in strong aqueous solution p-*urazine* $CO{<}\substack{NH\cdot NH\\ NH\cdot NH}{>}CO$ is formed Chattaway, Proc. Roy. Soc. 1908, A. 81, 381; hem. Soc. Trans. 1909, 95, 236; compare Datta, *ibid.* 1912, 101, 166).

Nitrocarbamide $NO_2\cdot NH\cdot CO\cdot NH_2$, prepared y the action of concentrated sulphuric acid n urea nitrate; it forms sparingly soluble rystals that decompose on melting; it is a trong acid, liberating acetic acid from its salts. he potassium, sodium and mercury salts have een prepared. On reduction with zinc dust nd sodium hydroxide, it forms *nitrosocarbamide* $H_2\cdot CO\cdot NH\cdot NO$, and this develops a purple olour with ferrous sulphate (Thiele and Lachnann, Annalen, 1895, 288, 281). On further eduction it yields semicarbazide

$$NH_2\cdot CO\cdot NH\cdot NH_2.$$

arbaminoazoimide $NH_2\cdot CO\cdot N_3$ from sodium itrite and semicarbazide has m.p. 92°–93° Thiele and Stange, Annalen, 1894, 283, 1).

The *alkyl* and *aryl* derivatives of urea are repared by Wöhler's method from the corresonding mono- or di- substituted ammonium anate: by the action of ammonia on the ocyanic ester, and by the action of carbonyl loride on the amine. For a description of ese derivatives, see Michler, Ber. 1875, 8, 64; Schiff, Annalen. 1877, 189, 157; Michler d Escherich, Ber. 1879, 12, 1162; Hemmelayr, Monatsh. 1891, 12, 89; Chancel, Compt. nd. 1892, 115, 242; Schneegans, Arch. Pharm. 94, 231, 675; A. E. Dixon, Chem. Soc. Trans. 1895, 47, 559; Diels and Golimann, Ber. 1911, 44, 3158; Cannizzaro, Gazz. chim. ital. 1871, 1, 41; Letts, Chem. Soc. Trans. 1872, 25, 448; Paternó and Spica, Gazz. chim. ital. 1875, 5, 388; Michler, Ber. 1876, 9, 396, 710; Claus, *ibid.* 693; Weith, *ibid.* 821; Pagliani, Gazz. chim. ital. 1879, 9, 28; Cosack, Ber. 1879, 12, 1449; 1880, 13, 1088; Michler and Zimmermann, *ibid.* 1881, 14, 2177; Michler and Keller, *ibid.* 2181; Traube, *ibid.* 1882, 15, 2122; Kym, *ibid.* 1890, 23, 424; Kühn and Landau, *ibid.* 811; Manuelli and Conanducci, Gazz. chim. ital. 1899, 29, ii. 136. For a summary of the alkyl substituted ureas, see Abderhalden's Biochemisches Handlexikon, 1911, vol. i. part 2, pp. 772, 773.

Urea forms condensation derivatives with *formaldehyde* (Goldschmidt, Ber. 1896, 29, 2438; Chem. Zeit. 1897, 21, 460; Di Palma, Boll. Chim. Farm. 1912, 51, 78; Einhorn and Hamburgher, Ber. 1908, 41, 24); with *β-diketones* (Evans, J. pr. Chem. 1892, [ii.] 45, 489); with *maleic anhydride* (Dunlap and Phelps, Amer. Chem. J. 1897, 19, 492); with *acetone* (Weinschenk, Ber. 1901, 34, 2185); with *ethyl oxalacetate* (Müller, J. pr. Chem. 1897, [ii.] 55, 505); with *hydrazine* (Curtius and Heidenreich, Ber. 1894, 27, 55) and with *phenylhydrazine* (Edeleanu, Chem. Zentr. 1892, i. 628).

*iso***Ureas**, *ψ-carbamides.* The tautomeric form of urea $HN:C(OH)NH_2$ is not known in the free state, but certain of its ethers have been prepared by the action of hydrogen chloride on cyanamide and the corresponding alcohol at 60°–70°. *Methyl* iso*carbamide* $HN:C(OMe)NH_2$ has m.p. 44°–45°, b.p. 82°/9 mm.; the *hydrochloride* melts at 130°; *ethyl*iso*carbamide* $HN:C(OEt)NH_2$ has m.p. 42°, b.p. 95°–96°/15 mm.; asym. *phenylmethylethyl*iso*carbamide* $HN:C(OEt)NMePh$ has b.p. 137°/21 mm., the isomeric asym. *phenylethylmethyl*iso*carbamide* $HN:C(OMe)NEtPh$ has b.p. 126°/15 mm. (Stieglitz and McKee, Ber. 1900, 33, 807); *propyl*iso*carbamidehydrochloride* melts at 64° and decomposes at 121° (Stieglitz and Noble, *ibid.* 1905, 38, 2243); sym. m-*nitrobenzoylphenyl*iso*carbamide methyl ether*

$$NO_2\cdot C_6H_4\cdot CO\cdot N:C(OMe)NHPh$$

has m.p. 124° (Bruce, J. Amer. Chem. Soc. 1904, 26, 419).

Thiourea. Isomerism amongst the derivatives of the sulphur analogue of urea is much more general than is the case with the derivatives of urea, and the convention has been adopted of limiting the term *thiocarbamides* to derivatives of the true thiocarbamide

$$H_2N\cdot CS\cdot NH_2\ ;$$

derivatives of the isomeric form $HN:C(SH)NH_2$ being called *thioureas*[1] (Reynolds, Chem. Soc. Trans. 1891, 59, 395).

Thiourea is prepared by heating ammonium thiocyanate at 160°–170°, the reaction is a balanced one; equilibrium is reached in about

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[1] To distinguish between the three isomeric forms of substituted derivatives of thiourea, Dixon (Chem. Soc. Trans. 1895, 67, 564) proposes to designate the NH and NH_2 attachments as *n* and *ν*, whilst if the sulphur attachment is occupied by the substituent the compound is designated a pseudothiourea. Thus, for example, the systematic names of $EtN:C(SH)NMe_2$, $NH:C(SMe)NH_2$ and $EtN:C(SMe)\cdot NHEt$ would be, respectively, *n*-ethyl-*ν*-dimethylthiourea, methyl-*ψ*-thiourea, and methyl-*ψ*-*nν*-diethylurea.

an hour, when the mixture contains about 25 p.c. of thiourea (Reynolds, Annalen, 1869, 150, 224; Reynolds and Werner, Chem. Soc. Trans. 1903, 83, 1; Findlay, *ibid.* 1904, 85, 403). Thiourea can also be obtained by the action of hydrogen sulphide on cyanamide

$$H_2N{\cdot}C\,\vdots\,N+H_2S=H_2N{\cdot}CS{\cdot}NH_2$$

(Baumann, Ber. 1875, 8, 26).

Thiourea crystallises in needles that melt at about 172° if rapidly heated; the true melting-point cannot be determined, owing to tautomeric change; it is probably above 177° (Findlay, *l.c.*).

Derivatives. The *nitrate* $CSN_2H_4{\cdot}HNO_3$, the *hydrochloride* $CSN_2H_4{\cdot}HCl$, and the *silver nitrate* derivative $CSN_2H_4{\cdot}AgNO_3$ are crystalline (Stevens, Chem. Soc. Proc. 1902, 17, 210; Kurnakow, Ber. 1891, 24, 3956). Dithiocarbamide dichloride $(CSN_2H_4)_2Cl_2$ can be crystallised from concentrated hydrochloric acid, and forms the *dinitrate* $(CSN_2H_4)_2(NO_3)_2$ by the action of dilute nitric acid; the *dibromide*

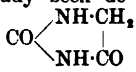
$$(CSN_2H_4)_2Br_2$$

and *di-iodide* $(CSN_2H_4)_2I_2$ are colourless and decompose on warming or by the action of solvents (Claus, Annalen, 1875, 179, 135; McGowan, Chem. Soc. Trans. 1886, 49, 190).

For the *alkyl* and *aryl* substituted derivatives of thiourea and thiocarbamide, see Arzruni, Ber. 1871, 4, 406; Miguel, Bull. Soc. chim. 1877, [ii.] 28, 104; de Clermont, Compt. rend. 1876, 82, 512; Blankenhorn, J. pr. Chem. 1877, [ii.] 16, 358; A. E. Dixon, Chem. Soc. Trans. 1891, 59, 562; 1892, 61, 536; 1893, 63, 318, 538; 1895, 67, 556; 1899, 75, 373; 1906, 89, 892; 1907, 91, 912; 1908, 93, 18. M. A. W.

UREASE *v.* FERMENTATION.

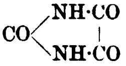
UREIDES or acyl derivatives of urea are formed by condensation between urea and the acid with the elimination of water; in the case of a monocarboxylic acid the product may be a *monoureide* $RCONH{\cdot}CO{\cdot}NH_2$ or a *diureide* $CO(NH{\cdot}COR)_2$, according as one or two molecules of the acid condense with one molecule of urea. Similar products may be obtained in the cases of the hydroxy acids and the di-carboxylic acids, but usually condensation occurs between one molecule of the acid and one of urea with the elimination of two molecules of a water and the formation of a *cyclic ureide.* The more important cyclic ureides have already been described; they include *glycolylurea*



$CO\left<\begin{array}{l}NH{\cdot}CH_2\\ \quad\ \ \vert\\ NH{\cdot}CO\end{array}\right.$

v. HYDANTOIN. *β-Lactylurea, hydracrylurea, hydrouracil* $CO\left<\begin{matrix}NH{\cdot}CH_2\\NH{\cdot}CO\end{matrix}\right>CH_2$ v. PYRIMIDINES.

Oxalylurea



$CO\left<\begin{array}{l}NH{\cdot}CO\\ \quad\ \ \vert\\ NH{\cdot}CO\end{array}\right.$

v. PARABANIC ACID. *Malonylurea* $CO\left<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right>CH_2$ v. *Barbituric acid*, art. PYRIMIDINES. *Hydroxymalonylurea, tartronylurea* $CO\left<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right>CH{\cdot}OH$ v. DIALURIC ACID. *Mesoxalylurea* $CO\left<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right>CO{\cdot}H_2O$ v. ALLOXAN. *Nitromalonylurea* $CO\left<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right>CH{\cdot}NO_2$ v. DILITURIC ACID. iso*Nitrosomalonylurea* $CO\left<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right>C{:}NOH$ v. *Violuric acid*, art. PYRIMIDINES. *Aminomalon- urea, aminobarbituric acid* $CO\left<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right>CH{\cdot}NE$ v. *Uramil*, art. PYRIMIDINES.

Of the open chain mono- and di- ureides, th following have been described: *formylur* $NH_2{\cdot}CO{\cdot}NH{\cdot}CHO$, m.p. 168°–169° (Geuth Marsh and Scheitz, Zeitsch. Chem. 1868, 30 Gorski, Ber. 1896, 29, 2046), forms a *mercu* salt (Matignon, Bull. Soc. chim. 1880, [ii.] 3 207); *acetylurea* $H_2N{\cdot}CO{\cdot}NH{\cdot}COCH_3$, m.p. 21 (Behrend, Annalen, 1885, 229, 30; Ber. 18 28, Ref. 63), forms *mercury, silver* and *cupro* salts (Matignon, *l.c.*); ab-*diacetylurea*

$$CO(NH{\cdot}COCH_3)_2,$$

m.p. 152°–153° (Schmidt, J. pr. Chem. 1872, 5, 63); *chloracetylurea* $NH_2{\cdot}CO{\cdot}NH{\cdot}COCH_2$ decomposes at 160° (Tommasi, Bull. Soc. chi 1873 [ii.] 19); *trichloracetylurea*

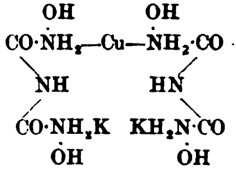
$$NH_2{\cdot}CO{\cdot}NH{\cdot}COCCl_3,$$

m.p. 150° with decomp. (Meldola and Tomma Chem. Soc. Trans. 1874, 404); *bromacetylur* $NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_2Br$; *tribromacetylurea*

$$H_2N{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CBr_3$$

m.p. 158° (Baeyer, Annalen, 1864, 130, 149 *cyanacetylurea* $H_2N{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_2CN$, m. 200°–210°; iso*valerylurea* $NH_2{\cdot}CO{\cdot}NH{\cdot}C_5H_9$ m.p. 191°; *monobromoisovalerylcarbam* $CHMe_2{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$ (*bromoural* m.p. 149°, is a narcotic (van der Eeckhou Arch. exp. Path. Pharm. 1907, 57, 338); *butyryl urea* $H_2N{\cdot}CO{\cdot}NH{\cdot}C_4H_7O$, m.p. 176°; *succiny urea* $C_4H_4O_2(NH{\cdot}CO{\cdot}NH_2)_2$; *benzoylur* $NH_2{\cdot}CO{\cdot}NHCOPh$, m.p. 200; ab-*dibenzoylur* $CO(NH{\cdot}COPh)_2$, m.p. 210°; aa-*dibenzoylur* $NH_2{\cdot}CO{\cdot}N(COPh)_2$, m.p. 197°.

Carbonyldiurea $CO(NH{\cdot}CO{\cdot}NH_2)_2$ decomposes on heating (Schmidt, J. pr. Chem. 187 [ii.] 5, 39); *carbonylurea, allophanic ac* $H_2N{\cdot}CO{\cdot}NH{\cdot}COOH$ does not exist in the fr state; the *methyl ester* has m.p. 208° (Ephrai Ber. 1893, 26, 2172), the *ethyl ester*, m.p. 19 (Liebig and Wöhler, Annalen, 20, 396; 59, 291 the *amide* $NH_2{\cdot}CO{\cdot}NH{\cdot}CONH_2,H_2O$ is *bur* m.p. 190°; it gives a purplish-violet col with copper sulphate and potassium hydrox due to the formation of the double salt



A similar reaction is given by proteids wh contain two amino groups in the molecu these groups being joined directly together through a single atom of nitrogen or carb The amino groups must be either two ·CONH groups or one $\cdot CONH_2$ group and one ·CSNH $C(NH)NH_2$, or $\cdot CH_2NH_2$ group. Substanc that are non-proteid in character but wh contain the necessary groups will also give t buiret reaction, for example, *oxamide* a *malonamide.*

Ureides of Sugars. The term *ureide* is applied to certain condensation product urea with aldehydes; these are of the ty $RCH{:}N{\cdot}CO{\cdot}NH_2$ and the most importan those derived from the aldoses. *Glucoseureide* $CH_2OH[CH\cdot OH]_4CH:N\cdot CO\cdot NH_2$, thick rhombic crystals, m.p. 207° (decomp.), $[\alpha]_D^{15}-23\cdot5^\circ$ in 10 p.c. aqueous solution; the *penta-acetyl derivative* $C_7H_9O_6N_2(CH_3CO)_5$ has m.p. 200°, and the *tetrabenzoyl* m.p. 117°. *Galactoseureide* is a white amorphous powder $[\alpha]_D+15^\circ$; *mannoseureide*, m.p. 188°, $[\alpha]_D^{20}-45\cdot8^\circ$; *lactoseureide* $(C_{12}H_{22}O_{10})N\cdot CO\cdot NH_2$ decomposes at 240°, $[\alpha]_D^{20}+2\cdot1^\circ$ (Schoorl, Rec. trav. chim. 1903, 22, 31; Mayer, Biochem. Zeitsch. 1909, 17, 145).

M. A. W.

URETHANE *v.* Synthetic drugs.

URETHANES are the esters of *carbamic acid* (*aminoformic acid*) $H_2N.COOH$; the free acid is not known. It is said to occur in blood serum (Drechsel, J. pr. Chem. 1875, [ii.] 12, 417; *cp.* Hofmeister, Archiv. Physiol. 1876, 12, 337), and in urine (Abel and Drechsel, Chem. Zentr. 1891, ii. 713; Hahn and Nencki. Arch. Sc. biol. Petersb. 1892, 1, 467; Abel and Muirhead, Arch. exp. Path. Pharm. 1893, 31, 15; 32, 467). The *ammonium* salt

$$NH_2\cdot COONH_4$$

is produced by the direct action of carbon dioxide on ammonia in cooled absolute alcohol. It is a white crystalline powder. The *sodium* $NaCH_2NO_2,H_2O$ and *potassium* KCH_2NO_2 salts are also crystalline; the *calcium* salt

$$Ca(CH_2NO_2)_2,H_2O$$

is insoluble in alcohol and crystallises from concentrated ammonia solution in four-sided prisms.

Carbamyl chloride, chloroformamide

$$Cl\cdot CO\cdot NH_2$$

prepared by passing hydrogen chloride over heated metallic cyanates, or carbonyl chloride over heated ammonium chloride, forms long, broad needles, m.p. 50°, b.p. 61°–62° (Gattermann and Schmidt, Ber. 1887, 20, 858).

Urethane, *ethyl carbamate* $NH_2\cdot COOEt$, prepared by the action of ammonia on ethyl carbonate or ethyl chlorocarbonate; by heating urea nitrate with alcohol; or by the action of alcohol on carbonyl chloride, crystallises in large pliable plates or prisms that break with a fibrous fracture, sublime readily, melt at 50° and boil at 184°.

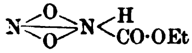
Urethane has therapeutic properties, being employed as a hypnotic. Certain of its substituted derivatives have similar properties; for example, *phenylurethane* or *euphorine*

$$PhHN\cdot COOEt$$

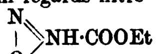
and *methylpropylcarbinol urethane* or *hedonal*

$$H_2N\cdot CO\cdot OCHMe\cdot CH_2\cdot CH_2\cdot CH_3.$$

Nitrourethane $NO_2\cdot NH\cdot COOEt$ melts at 64°, is readily soluble in water and alcohol and forms metallic salts, the *potassium*, *mercury* and *silver* having been prepared (Thiele and Lachmann, Annalen, 1895, 288, 304); from spectrochemical considerations. Brühl assigns the formula



to nitrourethane (Zeitsch. physikal. Chem. 1898, 26, 47; 25, 577). *Nitrosourethane* $NO\cdot NH\cdot COOEt$ melts and decomposes at 51°–52° and does not develop a purple colour with ferrous sulphate and potassium hydroxide; the *silver*, *potassium* and *ammonium* derivatives are yellow (Thiele and Lachmann, *l.c.*). From index of refraction values, Brühl regards nitrosourethane as diazourethane



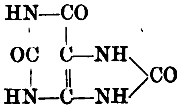
(Ber. 1902, 35, 1148), whilst Hantzsch formulates it as an *antidiazohydrate* $HO\cdot N:N\cdot COOEt$ (*ibid.* 1899, 32, 575). *Dibromourethane* $NBr_2\cdot COOEt$ has b.p. 100°–104°/10–11 mm. (Diels and Ochs, Ber. 1907, 40, 4571).

Urethane forms condensation products with aldehydes and keto acids. *Chloralurethane* $CCl_3\cdot CH(OH)NH\cdot COOEt$ has m.p. 103°; *bromalurethane* $CBr_3\cdot CH(OH)NH\cdot COOEt$ has m.p. 132° (Bischoff, Ber. 1874, 7, 628, 1078; Conrad and Hoëk, *ibid.* 1903, 36, 2206; Simon, Compt. rend. 1901, 133, 535; Simon and Chavanne, *ibid.* 1906, 143, 51).

Thiourethane, a mixture of the isomeric thiourethanes, is obtained by acting on an alcoholic solution of potassium thiocyanate with concentrated hydrochloric acid; these correspond with two of the isomeric forms of the hypothetical thiocarbamic acid, *ethyl xanthamide* $NH_2\cdot CS\cdot OEt$, has m.p. 38°, and *carbonylthioethylamine* $NH_2\cdot CS\cdot OMe$ (Blankenhorn, J. pr. Chem. 1877, [ii.] 16, 358).

M. A. W.

URIC ACID, 2 : 6 : 8-*trioxypurine*

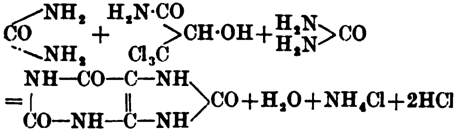


was discovered in human urine by Scheele in 1776 (Opuscula, 1776, 2, 73), independently by Bergmann in urinary calculi (*ibid.* 1776, 4, 232), and in 'chalk-stones' by Pearson in 1798 (Trans. Roy. Soc. 1798, 15).

Uric acid occurs in the urine of all animals, though only to a small extent in the case of herbivorous animals; the average daily excretion in normal man being 0·597 grm. (Hanzlik and Hawk, J. Biol. Chem. 1908, 5, 355). It occurs in the excrement of birds, reptiles, scaly amphibians, snails and insects; the wing scales of the group of butterflies known as the white *Pieridae* contain uric acid, those of the yellow *Pieridae* contain, as their pigment, a yellow derivative of uric acid, which can be obtained synthetically by heating uric acid with water in sealed tubes at a high temperature (Hopkins, Proc. Roy. Soc. 1894, 57, 5). Uric acid is a normal constituent of the organs and blood of birds, but only occurs in human blood under certain pathological conditions.

Preparation. Uric acid can be isolated from serpent's excrement, bird's excrement or guano by boiling the material with dilute alkali hydroxide or milk of lime, filtering the hot liquid and precipitating the uric acid by adding excess of hydrochloric acid to the filtrate. Uric acid can also be obtained from the yellow acid urates deposited from urine; this is boiled with sodium hydroxide until it ceases to evolve ammonia, the liquid is filtered and the acid sodium urate precipitated from the filtrate by means of carbon dioxide; this is redissolved in sodium hydroxide and the solution decomposed by acetic acid, or the hot solution of the alkali salt may be purified by boiling with a little potassium permanganate or dichromate and the filtrate decomposed by hydrochloric acid.

Synthesis. Uric acid was first synthesised by Horbaczewski by carefully fusing glycine with 10 to 15 times its weight of urea in small quantities at a time, until a considerable quantity of precipitate had formed in the molten mass; the uric acid was precipitated in the form of its sparingly soluble silver magnesium salt, which on treatment firstly with potassium sulphide and subsequently with hydrochloric acid, yielded pure uric acid (Monatsh. 1882, 3, 796; 1885, 6, 366). Further syntheses were effected by Horbaczewski (*ibid.* 1887, 8, 201) by fusing trichlorlactamide with 10 parts of carbamide

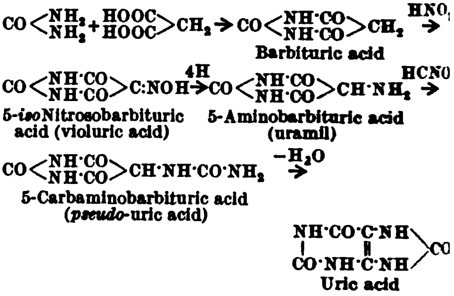


$$CO\left<\begin{matrix}NH_2\\NH_2\end{matrix}\right. + \begin{matrix}H_2N{\cdot}CO\\Cl_3C\end{matrix}\!\!>CH{\cdot}OH + \begin{matrix}H_2N\\H_2N\end{matrix}\!\!>CO$$

$$= \begin{matrix}NH-CO-C-NH\\ | \qquad\quad \| \\ CO-NH-C-NH\end{matrix}\!\!>CO + H_2O + NH_4Cl + 2HCl$$

and by fusing trichlorlactic acid or amino- acetic acid with carbamide (*ibid.* 1887, 8, 584).

In 1863, Baeyer (Annalen, 1863, 127, 3, 234) synthesised *pseudouric acid*, starting with malonic acid and carbamide; but it was not until 1895 that Fischer and Ach (Ber. 1895, 28, 2473) showed that uric acid could be readily obtained from pseudouric acid by fusion with oxalic acid or by boiling with hot dilute mineral acid (Fischer, *ibid.* 1897, 30, 559); a complete synthesis of uric acid from malonic acid and carbamide is therefore represented by the following equations:



$$CO\left<\begin{matrix}NH_2\\NH_2\end{matrix}\right. + \begin{matrix}HOOC\\HOOC\end{matrix}\!\!>CH_2 \rightarrow CO\left<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right>CH_2 \xrightarrow{HNO_2}$$

Barbituric acid

$$CO\left<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right>C{:}NOH \xrightarrow{4H} CO\left<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right>CH{\cdot}NH_2 \xrightarrow{HCNO}$$

5-*iso*Nitrosobarbituric acid (violuric acid) 5-Aminobarbituric acid (uramil)

$$CO\left<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}\right>CH{\cdot}NH{\cdot}CO{\cdot}NH_2 \xrightarrow{-H_2O}$$

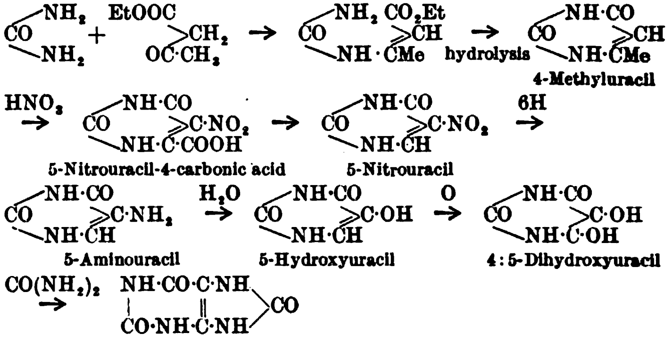
5-Carbaminobarbituric acid (*pseudo*-uric acid)

$$\begin{matrix}NH{\cdot}CO{\cdot}C{\cdot}NH\\ | \qquad\ \| \\ CO{\cdot}NH{\cdot}C{\cdot}NH\end{matrix}\!\!>CO$$

Uric acid

This is the most important synthetic method of preparing uric acid, and by replacing carbamide by its alkyl or aryl substituted derivatives, it is possible to prepare the corresponding alkyl or aryl substituted uric acids.

The synthesis of uric acid effected by Behrend and Roosen (Annalen, 1888, 251, 235), starting with ethyl acetoacetate and carbamide, is represented in the following series of equations:



4-Methyluracil

5-Nitrouracil-4-carbonic acid

5-Nitrouracil

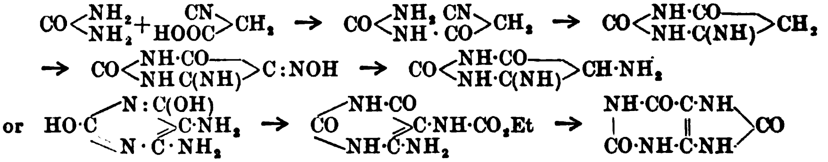
5-Aminouracil

5-Hydroxyuracil

4 : 5-Dihydroxyuracil

Uric acid

Traube's synthesis of uric acid, starting with cyanacetic acid and carbamide, is also important, and by substituting alkyl carbamides for carbamide, the method can be extended to the preparation of substituted uric acids. Cyanacetylcarbamide, prepared by the condensation of carbamide with cyanacetic acid, is converted by the action of alkali into 4-amino-2 : 6-dioxypyrimidine, from which 4 : 5-diamino-2 : 6-dioxypyrimidine is obtained by reducing its *iso*nitroso derivative; this diamine condenses with ethyl chloroformate to form a *urethane* derivative from the sodium derivative of which uric acid is produced by heating at 180°–190° (Ber. 1900, 33, 1375, 3035).



$$CO\left<\begin{matrix}NH_2\\NH_2\end{matrix}\right. + \begin{matrix}CN\\HOOC\end{matrix}\!\!>CH_2 \rightarrow CO\left<\begin{matrix}NH_2\ CN\\NH\cdot CO\end{matrix}\right>CH_2 \rightarrow CO\left<\begin{matrix}NH{\cdot}CO\text{——}\\NH{\cdot}C(NH)\end{matrix}\right>CH_2$$

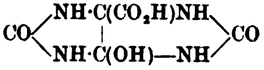
$$\rightarrow CO\left<\begin{matrix}NH{\cdot}CO\text{——}\\NH\,C(NH)\end{matrix}\right>C{:}NOH \rightarrow CO\left<\begin{matrix}NH{\cdot}CO\text{——}\\NH{\cdot}C(NH)\end{matrix}\right>CH{\cdot}NH_2$$

Properties. Pure uric acid forms a colourless microcrystalline powder consisting of rhombic transparent plates or prisms; as precipitated from urine or guano extracts, the crystals are yellowish red or brown. These exhibit, under the microscope, characteristic irregularities in form, due to the rounding of the obtuse angles of the rhombic prisms, and the interpenetration of the crystals, and present the form of dumb-bells, whetstones, rosettes of prismatic crystals, six-sided irregular plates or rectangular plates with partly jagged sides.

Uric acid is odourless and tasteless; it is sparingly soluble in water, one part dissolving in 39.480 parts at 18° (His and Paul, Zeitsch. physiol. Chem. 1900, 31, 41), or 15,505 parts at

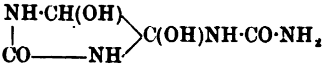
37^c (Gudzent, *ibid.* 1909, 60, 27). When shaken with water, uric acid decomposes so that the solubility tends to increase with the time; the increase is only noticeable at the end of 24 hours and then rises rapidly until at the end of 10 days the solubility is 11 times as great as at the end of a few hours, and in the same time the electrical conductivity has increased 55 times (Gudzent, *l.c.*). The molecular electrical conductivity of a saturated solution of uric acid is 32·24 at 18° (His and Paul, *l.c.*) or 33·92 at 37° (Gudzent, *l.c.*); the dissociation constant $k=0{\cdot}000151$ at 18° or 0·000233 at 37°. Uric acid is fairly readily soluble in lactic acid, acetic acid or warm concentrated sulphuric acid. It dissolves in glycerol, but is insoluble in alcohol or ether; it dissolves readily in aqueous solutions of alkali hydroxides, of lithium carbonate, and of certain organic bases such as ethylamine, propylamine, piperazine, but is only sparingly soluble in solutions of urotropine (hexamethylenetetramine), lycetol (piperazine tartrate) or ammonia (Stevens and May, J. Amer. Chem. Soc. 1911, 33, 434).

Uric acid is not volatile: on being strongly heated it breaks up into urea, hydrocyanic acid, cyanuric acid and ammonia (Wöhler, Pogg. Ann. 1839, 15, 529, 619). When oxidised by strong nitric acid or potassium chlorate and hydrochloric acid, or by chlorine or bromine water in the cold, uric acid is broken down into alloxan (mesoxalylcarbamide) (*q.v.*) and urea; warm dilute nitric acid produces parabanic acid (oxalylcarbamide) (*q.v.*). By the action of such oxidising agents as potassium permanganate, or ferricyanide, lead peroxide, mercuric oxide or ozone in neutral or alkaline media, uric acid yields carbon dioxide and allantoin (glyoxyldiureide) (*q.v.*). According to Behrend (Annalen, 1904, 333, 141) and Behrend and Schultz (*ibid.* 1909, 365, 21), the first product of oxidation of uric acid in alkaline media is *hydroxyglycolurilcarboxylic acid*



$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH{\cdot}C(CO_2H)NH}\\ \qquad\quad |\\ \mathrm{NH{\cdot}C(OH){-}NH}\end{array}\right\rangle\mathrm{CO}$$

This is next converted into the *compound*



$$\left.\begin{array}{l}\mathrm{NH{\cdot}CH(OH)}\\ |\\ \mathrm{CO{-\!-\!-}NH}\end{array}\right\rangle\mathrm{C(OH)NH{\cdot}CO{\cdot}NH_2}$$

which, on acidifying with acetic acid, yields carbon dioxide and allantoin. On heating with an excess of alkali hydroxide, hydroxy glycolurilcarboxylic acid takes up the elements of water, forming *uroxamic acid* (*dicarbaminomalonic acid*)

$$\mathrm{(COOH)_2C(NH{\cdot}CO{\cdot}NH_2)_2}$$

(*q.v.*). When oxidised by hydrogen peroxide in alkaline solution, uric acid yields *tetracarbonimide* $\mathrm{CO}\!\left\langle\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO{\cdot}NH}\end{array}\right\rangle\!\mathrm{CO}$ (Scholtz, Ber. 1901, 34, 4130), *carbonylcarbamide* $\mathrm{CO(NH{\cdot}CO{\cdot}NH_2)_2}$ and *carbamide* (Schittenhelm and Wiener, Zeitsch. physiol. Chem. 1909, 62, 100).

Uric acid is decomposed when fused with potassium hydroxide, yielding the potassium salts of prussic, cyanic, carbonic and oxalic acids. When heated under pressure at 160°–170° with concentrated hydrochloric or hydriodic acids, it yields carbon dioxide, ammonia and glycocoll; it is oxidised by a solution of copper oxide in ammonia (Schweizer's reagent) in the presence of potassium hydroxide to urea and oxalic acid, and a similar oxidation is effected by boiling with ferric chloride.

For the physiological properties of uric acid, its origin, and the rôle it plays in the animal economy, see Article URINE; also Biochemisches Handloxikon von Abderhalden, vol. iv. 1095–1106; and Oxidations and Reductions in the Animal Body, by H. D. Dakin, 92.

Detection. Uric acid is readily identified by the appearance of the crystals under the microscope. The most characteristic and delicate test for uric acid is the 'murexide test,' which is applied as follows: a few drops of strong nitric acid is added to the uric acid or urate and the solution evaporated to dryness on the water bath, preferably in a porcelain basin, a yellowish red residue of alloxantin is obtained which acquires the rich purple colour of ammonium purpurate (*murexide, q.v.*) on moistening with ammonia, the colour changing to blue on the addition of sodium hydroxide. The nitric acid employed in the test may be replaced by chlorine or bromine water, or by a few drops of concentrated hydrochloric acid and a small crystal of potassium chlorate. Other colour reactions of uric acid are described by (1) Denigès (J. Pharm. Chim. 1888, [v.] 18, 161), the uric acid is oxidised to alloxan by evaporating a solution in dilute nitric acid; on adding successively to the residue a few drops of concentrated sulphuric acid and of benzene containing thiophen, a bluish coloration is obtained; (2) Ganassini (Boll. chim. farm. 1908, 47, 715), the uric acid or urate is suspended in water and dissolved in 10 p.c. sodium hydroxide; subsequent saturation of the solution with potassium persulphate and the gradual addition of 10 p.c. zinc sulphate solution, until the precipitate formed no longer redissolves, causes the precipitate to assume a bluish-green colour. This test is not disturbed by the presence of proteins, other purines or pyrimidines, and may be applied for the detection of uric acid in urine or in blood. According to Vitali (*ibid.* 1911, 50, 799), sodium peroxide is the only oxidising agent that can replace the potassium persulphate in the above test, and no other metallic salt can be used instead of the zinc salt. (3) Folin and Denis (J. Biol. Chem. 1912, 12, 239), a blue coloration is developed when a solution containing 1 mg. of uric acid is mixed with 2 c.c. of a solution prepared by boiling for two hours a mixture of 100 grms. sodium tungstate, 80 c.c. of 85 p.c. phosphoric acid, and 750 grms. of water, cooling and diluting to a litre (compare Leturc, Ann. Chim. anal. 1907, 12, 194). Tests based upon the reducing properties of uric acid are the formation of a yellow, brown, or black stain of silver, when filter paper previously moistened with silver carbonate is treated with a drop of a solution of uric acid in sodium carbonate; and the reduction of Fehling solution on boiling an alkaline solution of uric acid with excess of the reagent. For the detection of uric acid in blood, Weber (Pharm. Zeit. 1912, 57, 252) recommends the following method: the blood is treated with sodium chloride and potassium phosphate to remove the proteins, the filtrate evaporated to a small bulk and saturated with ammonium chloride, the uric acid is thus precipitated as ammonium urate, which is collected and treated with a few drops of hydrochloric acid and the crystals of uric acid identified under the microscope or by the murexide test.

Estimation. The methods of estimating uric acid in urine are based upon the precipitation of the uric acid in the form of the sparingly soluble ammonium or the double silver magnesium salt, and the subsequent determination of the uric acid in the carefully washed precipitate. Hopkins' method (Proc. Roy. Soc. 1892, 52, 93; J. Path. and Bacteriology, 1893, 1, 451), 30 grms. of ammonium chloride are added to 150 c.c. of the filtered urine previously warmed to 40° to 45°, after about an hour the precipitate of ammonium urate is collected on a small filter, washed with a 10 p.c. solution of ammonium sulphate until free from chlorine, and transferred to a beaker by means of a jet of hot water, the solution cooled and diluted with water to 100 c.c., 20 c.c. of pure concentrated sulphuric acid are added, and N/20 potassium permanganate run into the acid liquid at 60° until it acquires a pink tint permanent for some seconds and not changed by stirring. Each c.c. of N/20 permanganate solution decolorised represents 0·00375 grm. of uric acid.

Wörner (Zeitsch. physiol. Chem. 1900, 29, 70) recommends decomposing the washed ammonium urate with 1–2 p.c. sodium hydroxide solution, heating the solution on the water-bath until it ceases to evolve ammonia and then determining the nitrogen in the residue by the Kjeldahl method; 1 c.c. N/10 sulphuric acid corresponds with 0·0042 grm. uric acid.

Folin and Shaffer's modification of Hopkins' method (Zeitsch. physiol. Chem. 1901, 32, 552) is as follows: A solution containing 500 grms. of ammonium sulphate, 5 grms. uranium acetate, and 10 p.c. acetic acid, 60 c.c. per litre is prepared, and 75 c.c. of this solution are mixed with 300 c.c. of the urine, kept for five minutes, passed through a double filter and two quantities of 125 c.c. each collected. Five c.c. of concentrated ammonia are added to each and after about 12 hours the precipitates of ammonium urate are collected and washed and the uric acid in each estimated by the permanganate method. The addition of uranium acetate is made in order to precipitate a small quantity of protein material which is otherwise thrown down on the addition of the ammonia, and which reduces permanganate.

Salkowski's method modified by Ludwig (Chem. Zentr. 1891, 390) consists in precipitating the uric acid in the urine (100 to 200 c.c.) with a mixture of ammoniacal silver solution and magnesia mixture; the precipitate containing all the uric and phosphoric acids is filtered and washed with very dilute ammonia. It is then decomposed by a warm dilute solution of potassium sulphide forming potassium urate which passes into solution, the filtrate is acidified with hydrochloric acid, evaporated to a small bulk, and the uric acid that separates on cooling is collected on a tared filter, washed with water, alcohol, ether, carbon disulphide, and again with ether, dried at 110° and weighed.

Folin and Shaffer (Zeitsch. physiol. Chem. 1901, 32, 552) recommend the following modification of the method in order to facilitate the removal of the silver from the silver magnesium urate: the double salt is decomposed by sulphuretted hydrogen in an acid solution containing 5 to 10 c.c. of 1 p.c. copper sulphate solution and the liquid boiled for a few minutes before filtering.

Derivatives. *Salts.* Uric acid behaves as a feeble dibasic acid and forms three series of salts, the *normal* urates of the type

$$Na_2C_5H_2O_3N_4$$

are readily soluble in water and are never found in the animal system; the *acid* or *diurates* $NaC_5H_3O_3N_4$ are sparingly soluble and occur pathologically in gouty concretions; and the *quadri-* or *hemi-urates*

$$NaC_5H_3O_3N_4,C_5H_4O_3N_4$$

are more readily soluble than the diurates and are the common form in which uric acid occurs physiologically.

Normal urates may be obtained by dissolving uric acid in the theoretical quantity of alkali. They are alkaline in reaction and are decomposed by carbon dioxide, forming the acid salt. The *potassium* salt $K_2C_5H_2O_3N_4$ is crystalline; it dissolves with partial decomposition into the acid salt in about 36 parts of cold water; the *sodium* salt $Na_2C_5H_2O_3N_4,H_2O$ is less soluble than the potassium salt; the *calcium*

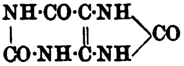
$$CaC_5H_2O_3N_4,$$

strontium $SrC_5H_2O_3N_4,2H_2O$, *barium*

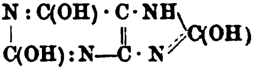
$$BaC_5H_2O_3N_4,H_2O,$$

and *lead* $PbC_5H_2O_3N_4$ salts are sparingly soluble. The *mercury* salt $C_5H_2O_3N_4Hg$ is a white amorphous precipitate; it does not give mercuric oxide with sodium hydroxide solution and is therefore probably a lactam salt (Auld, Chem. Soc. Trans. 1907, 1046).

Acid or *di-urates.* According to Gudzent (Zeitsch. physiol. Chem. 1909, 60, 38), uric acid forms two series of primary metallic salts (mono-sodium, potassium and ammonium urates), which differ as regards solubility. The salts of the *a*-series cannot be obtained pure, as at the moment of formation in water they tend to pass into the salts of the *b*-series. The probable cause of the change is an intramolecular rearrangement, so that the two series correspond with the two tautomeric forms of uric acid



Lactam



Lactim

The unstable *a*-salts are probably the *lactam* urates, and the stable *b*-salts the *lactim* urates. The *a*-salts have solubilities and specific conductivities that at 18° are some 33·4 p.c., or at 37° some 33·9 p.c. greater than the corresponding values for the more stable *b*-salts.

The *sodium* salt $NaC_5H_3O_3N_4,1\frac{1}{2}H_2O$ forms a crystalline powder soluble in 1200 parts of cold or 120 parts of boiling water, forming a neutral solution; the *potassium* salt

$$KC_5H_3O_3N_4$$

is amorphous and dissolves in 800 parts of cold or 70–80 parts of boiling water; *lithium* salt $LiC_5H_3O_3N_4$ forms crystalline grains and is soluble in 370 parts of cold or 39 parts of boiling water; the *ammonium* salt $NH_4C_5H_3O_3N_4$ is soluble in 1500 parts of cold water and quite insoluble in saturated solutions of ammonium chloride or sulphate; and the *magnesium* $(C_5H_2O_3N_4)_2 2Mg,6H_2O$, *calcium*

$$(C_5H_2O_3N_4)_2Ca,2H_2O,$$

strontium $(C_5H_2O_3N_4)_2Sr,2H_2O$, *barium*

$$(C_5H_2O_3N_4)_2Ba,3H_2O,$$

and *lead* $(C_5H_2O_3N_4)_2Pb$ salts are described.

The *quadri-urates* are difficult to obtain pure as they readily break down into diurates and uric acid; according to Rosenheim (Zeitsch. physiol. Chem. 1911, 71, 272) and Kohler (*ibid.* 70, 360) the quadriurates are only mixtures, in molecular proportions, of primary urates and uric acid; they are stated to exist normally in the urine and constitute the whole of the urinary excretion of birds and reptiles (*v.* URINE).

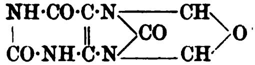
Adrenaline urate $C_9H_{13}O_3N{\cdot}C_5H_4O_3N_4$ forms small pointed plates (Pauly, Ber. 1904, 37, 1388). *Piperazine urate* $C_4H_{10}N_2,C_5H_4O_3N_4$ is soluble in 50 parts of water at 17°.

Uric acid forms the following condensation products with formaldehyde:—

Diformaldehyde-uric acid $C_5H_4N_4O_3,2CH_2O$ is a crystalline, sparingly soluble compound, monobasic towards N/3 sodium hydroxide and forms a *barium* and a *calcium* salt (Weber, Pott and Pollens, Ber. 1897, 30, 2514; Annalen, 1898, 299, 340). *Formaldehyde uric acid*

$$C_5H_4O_3N_4,CH_2O$$

crystallises in needles or prisms, decomposes at 37°, and forms crystalline alkali salts; and *anhydroformaldehyde-uric acid*



formed by dissolving diformaldehyde-uric acid in concentrated sulphuric acid and pouring the solution into ice water (Nicolaier, Chem. Zentr. 1907, i. 949). M. A. W.

ψ-URIC ACID *v.* PYRIMIDINES.

URIDINE *v.* PYRIMIDINES.

URINE. The kidneys are compound tubular glands, and possess the power of excreting from the blood certain waste products which in aqueous solution constitute the urine. Its most important constituents are the result of the breakdown of nitrogenous materials in the body, but these substances, urea, uric acid, &c., are not actually formed in the kidneys themselves. The liver is the most important organ for their actual formation; the kidney is merely the situation where they find an exit from the body.

The characters of the urine differ greatly in different parts of the animal kingdom, according to the character of the food ingested, and the different metabolic habits of animals. The most striking difference is seen when one compares the liquid urine of mammals (in which urea is the main substance in solution) and the semi-solid urine of birds and snakes, in which urates form the preponderant constituents. In the following account attention will be in the main directed to the urine which is most familiar, namely that of man and other mammals.

A man of average weight and height, taking a normal mixed diet, passes from 1400 to 1600 c.c. (about 50 oz.) daily, and this contains about 50 grms. (1¾ oz.) of solids. Its yellow colour varies considerably with the concentration of the urine, and is due to the presence of a number of pigments, of which *urochrome* (an amorphous nitrogenous substance of doubtful composition, originally so named by Thudichum) is the most abundant. Another named *urobilin*, a derivative of the bile pigment, is present in health in small quantities, but may be considerably increased in certain diseases.

The reaction of urine is acid; this is partly due to free acid, but mainly to acid salts, of which acid sodium phosphate is the most abundant. During digestion, however, there is a formation of free hydrochloric acid in the stomach, and a corresponding liberation of bases in the blood causes the urine to be less acid, or even alkaline. Alkaline urine is also seen in herbivorous animals and vegetarians; here the food contains excess of alkaline salts of acids such as tartaric, citric, malic, &c. These acids in the body are oxidised into carbonates which, passing into the urine, give it an alkaline reaction.

The specific gravity varies inversely as the quantity of urine passed; the quantity depends on the amount of water ingested, and also on the amount of water that leaves the body by other channels, such as the skin. It varies normally from 1·015 to 1·025. A sp.gr. below 1·010 should excite suspicion of hydruria; one over 1·030 of a febrile condition, or of diabetes, in which disease it may rise to 1·050. The sp.gr. has, however, been known to sink as low as 1·002 (after large potations, *urina potus*), or to rise as high as 1·035 (after great sweating) in perfectly healthy people.

The following table gives the average amounts of the urinary constituents passed by a man taking an ordinary diet containing about 100 grams. of protein in the 24 hours—

Total quantity of urine	1500	grms.
Water	1400	„
Solids	60	„
Urea	35	„
Creatinine	0·9	„
Uric acid	0·75	„
Hippuric acid	1·0	„
Ammonia	0·65	„
Sodium chloride	16·5	„
Phosphoric acid	3·5	„
Sulphuric acid	2·0	„
Chlorine	11·0	„
Potassium	2·5	„
Sodium	5·5	„
Calcium	0·26	„
Magnesium	0·21	„

The most abundant constituents are, therefore, water, urea, and sodium chloride. We will take the most important individual constituents one by one.

Urea or **carbamide** $CO(NH_2)_2$ is isomeric with ammonium cyanate, from which it was first prepared synthetically in 1828 by Wöhler. Wöhler's observation derives interest from the fact that this was one of the first organic substances prepared synthetically by chemists.

It crystallises in the dimetric system, and is readily soluble in water and in alcohol; it has a faint saltish taste, and is neutral to litmus. When treated with nitric acid, octahedra, or lozenge-shaped tablets are formed of urea nitrate $(CON_2H_4{\cdot}HNO_3)$; when treated with oxalic acid prismatic crystals of urea oxalate

$$[CO(NH_2)_2]_2{\cdot}C_2H_2O_4$$

are formed.

Under the influence of certain micro-organisms which grow readily in stale urine, it is converted into ammonium carbonate

$$[CON_2H_4+2H_2O=(NH_4)_2CO_3].$$

Hence the ammoniacal odour of putrid urine. In the soil the urinary ammonia is converted into nitrates by nitrifying organisms (*see* SOILS).

By means of nitrous acid, urea is broken up, as shown in the following equation

$$CON_2H_4+2HNO_2=CO_2+3H_2O+2N_2.$$

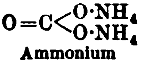
Sodium hypobromite decomposes urea as follows

$$CON_2H_4+3NaBrO=CO_2+N_2+2H_2O+3NaBr.$$

This reaction is important, for on it one of the readiest methods for estimating urea depends. If the hypobromite is mixed with excess of sodium hydroxide, the carbon dioxide is absorbed, and nitrogen is the only gas evolved; this is collected in a suitable measuring tube, and from its amount, the quantity of urea is easily calculated.

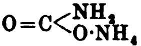
More accurate determinations may, however, be made by the methods of Mörner and Sjöquist, or of Folin (*v.* UREA). The former consists in treating the urine with a mixture of barium chloride, barium hydroxide, ether, and alcohol; all nitrogenous substances, except urea, are thus precipitated, and the nitrogen in the filtrate and washings is estimated by Kjeldahl's method. The latter method (Folin's) depends on the fact that urea is decomposed into ammonia and carbon dioxide by boiling with magnesium chloride in the presence of hydrochloric acid. The ammonia is estimated by distilling it into standard acid and subsequent titration. From the total ammonia so found, that preformed has to be deducted, and this amount is ascertained in another specimen of the same urine.

The quantity of urea is practically uninfluenced by muscular work, but depends mainly on the amount of protein ingested. The amino acid fragments formed by the digestion of protein are utilised in two ways. A small portion is used by the tissue cells to repair their waste. In time this will be catabolised and the waste products discharged as urea, ammonia, creatinine, &c. The amount of such *endogenous* metabolism is constant. The other and larger part of the cleavage products of the food protein are deamidised and converted into urea by the liver, the non-nitrogenous fatty residue being burnt, and so utilised as a source of heat and other forms of energy. This part of metabolism is termed *exogenous*. Urea excretion is usually at a maximum about 3 hours after a meal. The conversion of amino acids into urea is, in part at any rate, due to enzymic action; *e.g.* arginase is an enzyme which converts arginine (one of the more complex amino acids resulting from protein disintegration) quantitatively into urea and ornithine (di-amino-valeric acid). There is also no doubt that ammonia is an important intermediate between such amino acids as glycine (amino-acetic acid), leucine (amino-caproic acid), &c., and the final product urea. Ammonia so liberated unites with the carbon dioxide of the blood, and ammonium carbonate and carbamate are thus formed. The close relationship of these two salts to urea is apparent from their formulæ—



$$O=C<\begin{matrix}O{\cdot}NH_4\\O{\cdot}NH_4\end{matrix}$$

Ammonium carbonate.



$$O=C<\begin{matrix}NH_2\\O{\cdot}NH_4\end{matrix}$$

Ammonium carbamate.

$$O=C<\begin{matrix}NH_2\\NH_2\end{matrix}$$

Urea or carbamide.

A small quantity of ammonia always slips through into the urine, because a small quantity of the ammonia-containing blood passes through the kidney before reaching the organ (the liver), which is capable of converting it into urea. Acids are very toxic to the body, and the defence of the body against acids (administered as such, or produced in pathological metabolism, *e.g.* fatty acids in diabetes) is an increase of ammonia formation, or to put it more correctly, less of the ammonia formed is converted into urea.

Creatine and *creatinine*. Creatine is an abundant constituent of muscular tissue; *in vitro* by boiling it with baryta it takes up water and splits up into urea and methyl-glycine, as shown in the following equation—

$$C_4H_9N_3O_2+H_2O=CON_2H_4+CH(CH_3)NH_2{\cdot}COOH.$$

Creatine, however, is absent from normal urine, and only occurs in starvation and in other conditions, in which there is a rapid loss of muscular tissue. Its normal fate in the body is unknown, since creatine injected into the circulation leaves the body in the urine unchanged, and leads to no increase of urea.

It also is not converted into creatinine, which was formerly held to be its fate. Here, again, we have an instance of reactions, which occur *in vitro*, but not *in vivo*. Creatinine is a crystalline, strongly basic substance, which chemically is creatine *minus* a molecule of water. It is always present in the urine, and next to urea, is its most abundant nitrogenous constituent. Mellanby believes that certain products of protein catabolism, the nature of which is uncertain, are carried to the liver, and from these the liver forms creatinine; this is transported to the muscles, and there stored as creatine, excess being then eliminated in the urine. The small amount of creatinine excreted in liver disease favours the view that the liver is the great agent in its production, as it is in that of urea and uric acid. In health the amount of creatinine is very constant, and is not influenced by diet or muscular exercise.

Uric acid ($C_5H_4N_4O_3$) is excreted as urates in mammals in small quantities only, but in birds and serpents is the principal nitrogenous constituent of their urine. It can be readily prepared from the latter urine, in which it is mainly present as the acid ammonium urate, by dissolving it in sodium hydroxide and precipitating with hydrochloric acid. It crystallises in rectangular plates and prisms. It requires for its solution 1900 parts of hot, and 15,000 parts of cold, water. On oxidation it yields urea and oxalic acid, alloxan ($C_4H_2N_2O_4$) or allantoin ($C_4H_6N_4O_3$), being intermediate products, according to the oxidising agent employed. It can be best identified by the *murexide* reaction, which consists in evaporating to dryness with nitric acid; the yellowish-red residue gives, on the addition of ammonia, the violet ammonium purpurate.

Uric acid is dibasic, and forms two classes of salts, which may be exemplified by the acid sodium urate ($C_5H_3NaN_4O_3$) and the normal sodium urate ($C_5H_2Na_2N_4O_3$). The first-named of these salts is the chief constituent of the urate deposit which often occurs in concentrated urine.

If uric acid is represented by H_2U, the normal urates may be written M_2U, and the acid urates MHU. Bence-Jones, and later Sir W. Roberts, considered that the urates actually occurring in the urine are quadriurates

$$MHU{\cdot}H_2U.$$

There is no doubt that such compounds do not actually exist. It has been suggested that the mixture of urate and uric acid is of the nature of "solid solution." Uric acid is best estimated by Hopkins' method, which briefly consists in saturating the urine with an ammonium salt; ammonium urate thus precipitated is dissolved in alkali and titrated with standard potassium permanganate until a diffused pink-blush appears throughout the solution.

In birds uric acid originates from the combination of ammonia and lactic acid. In mammals it mainly arises from the purine bases of the food, or which are cleavage products of nucleic acid, the main constituent of the nuclei of the body cells. In this process several tissue enzymes come into play; first nuclease liberates adenine (amino-purine $C_5H_3N_4{\cdot}NH_2$) and guanine (amino-oxypurine $C_5H_3N_4O{\cdot}NH_2$) from nucleic acid; then 'deamidising' enzymes convert adenine into hypoxanthine (monoxypurine $C_5H_4N_4O$) and guanine into xanthine (dioxypurine $C_5H_4N_4O_2$); oxidases step in next and convert hypoxanthine into xanthine, and xanthine into uric acid (trioxypurine $C_5H_4N_4O_3$). The liver is the principal seat of these transformations, and in some animals some of the uric acid so formed is destroyed in the same organ, and appears as allantoin and urea. So far as tissue extracts can give a true picture of metabolism *in vivo* the human tissues are destitute of the uricolytic (uric acid destroying) enzyme.

Small quantities of purine bases are found in the urine in addition to uric acid.

Hippuric acid ($C_9H_9NO_3$) in the form of hippurates is present in small quantities in the urine of man, but is specially characteristic of herbivorous urine. This is due to the food of herbivora containing substances of the benzoic acid group. The condensation of benzoic acid with glycine to form hippuric acid appears to occur in the kidney itself, and may be represented by the following equation—

$$\underset{\text{Benzoic acid.}}{C_6H_5{\cdot}COOH} + \underset{\text{Glycine.}}{CH_2(NH_2)COOH}$$

$$= \underset{\text{Hippuric acid.}}{CH_2(NH{\cdot}CO{\cdot}C_6H_5)COOH} + H_2O.$$

Kynurenic and **urocanic acids** are present in small quantities in dog's urine. Kynurenic acid $C_{10}H_7NO_3$ is hydroxyquinoline-carboxylic acid ($HO{\cdot}C_9H_5N{\cdot}COOH$) and originates from one of the decomposition products of protein called tryptophan (indole-amino-propionic acid). Urocanic acid ($C_{12}H_{12}N_4O_4$) is a rarer constituent, and its origin in the body is not clear.

Inorganic constituents of urine. The principal salt is *sodium chloride*, and its amount varies with that in the food. The *sulphates* present are principally those of sodium and potassium. They are derived from the metabolism of protein, and their excretion, although it occurs earlier than that of urea, runs parallel with it. About one-tenth of the total sulphates are ethereal sulphates, such as potassium phenyl sulphate and potassium indoxyl sulphate (urinary indican); the organic radicles originate from protein putrefaction in the alimentary canal, and abnormally great putrefactive processes there lead to an increase in the excretion of such sulphates. Sulphur is also present in the form of less highly oxidised organic compounds, usually spoken of as 'neutral sulphur,' a term which includes thiocyanic acid and its salts, taurine, cystine, methyl mercaptan. A number of other substances also are present in minute quantities.

Carbonates are only present in alkaline urine. Alkaline and earthy *phosphates* are also present and small quantities of organic phosphates, for instance, glycero-phosphates. They arise partly from the food, but chiefly from the metabolism of organic phosphorised constituents of the body, such as nucleic acid, lecithin, and other phosphorised fats (phosphatides).

Abnormal constituents of urine. The most commonly occurring of these are albumin (in Bright's disease) and other proteins, dextrose, acetone, aceto-acetic acid, and β-hydroxybutyric acid in diabetes, lactose in nursing mothers, bile in jaundice, blood when hæmorrhage occurs in any part of the urinary tract, hæmoglobin, and certain derivatives of hæmoglobin in black water fever and other pathological states, and pus as the result of suppuration in any part of the urinary tract.

Urinary deposits. Normal urine is clear except for a faint cloud of mucus. Formed or anatomical elements such as blood corpuscles, pus corpuscles, bacteria, entozoa, &c., may be present in various pathological conditions, and are identified by microscopic examination. A special chemical interest attaches, however, to crystalline deposits, and without entering into any discussion of the medical reasons that lead to their appearance, these may be briefly enumerated as follows:—

A. In acid urine, may be found—

1. Uric acid, as whetstone, dumb-bell, or sheaf-like aggregations of crystals deeply tinged with urinary pigment, looking like cayenne pepper.

2. Urates. These are generally amorphous. The acid urate of sodium and ammonium may sometimes occur in star-shaped clusters of needles or spheroidal clumps with projecting spines. The deposit has the appearance of brick-dust, as it is coloured by one of the urinary pigments (uroerythrin). This deposit dissolves on warming the urine.

3. Calcium oxalate in the form of octahedral crystals insoluble in acid.

4. Cystine (diamino-dithio-lactic acid

$$C_6H_{12}N_2S_2O_4)$$

in colourless hexagons; a rare condition often hereditary.

5. Calcium phosphate $CaHPO_4,2H_2O$, rare.

6. Leucine (*amino-caproic acid*) and tyrosine βp-*hydroxyphenyl-a-aminopropionic acid*), rare.

B. In alkaline urine we may find—

1. Phosphates; calcium phosphate

$$Ca_3(PO_4)_2,$$

which is amorphous, triple phosphate

$$MgNH_4PO_4,6H_2O$$

in 'coffin lid' crystals or feathery stars, calcium hydrogen phosphate $CaHPO_4$ in rosettes, spherules, or dumb-bells; magnesium phosphate $Mg_3(PO_4)_2$ in long plates. All are soluble in acetic acid without effervescence.

2. Calcium carbonate $CaCO_3$, biscuit-shaped crystals, common in herbivorous urine, soluble in acetic acid with effervescence.

3. Ammonium urate $C_5H_2(NH_4)_2N_4O_3$ 'thorn apple' spherules.

4. Leucine and tyrosine, very rare.

Of these deposits, urates in acid urine, and phosphates in alkaline urine are the commonest; these are not necessarily pathological; thus urates may form in the urine when it cools, especially if that secretion is concentrated, *e.g.* after sweating profusely. Urine, when it becomes alkaline, always deposits phosphates, and the alkaline urine of herbivora is always thick for that reason.

Urinary calculi. Concretions called sand, gravel, and stones, according to their size, may form in the kidney, the ureter, or in the bladder. They result from the conglomeration of urinary deposits, the deposition occurring in concentric layers. The substances deposited in acid urine are most frequently uric acid, urates or calcium oxalate, or a mixture of these materials; in alkaline urine, phosphates. If the reaction of the urine changes during the formation of the calculus alternate layers of these two sets of materials will be found. The uric acid calculus is generally regarded as the commonest form of stone in the bladder, but in renal calculi, as B. Moore has shown, the most abundant constituent is calcium oxalate, frequently mixed with calcium phosphate, the second constituent in frequency and abundance. Calcium is practically the only base associated with oxalic acid, phosphoric acid, and in less amount with uric acid. All these acids form highly insoluble salts with calcium. Oxalic and uric acids are associated products in metabolism, and occur in cases of incomplete oxidation.

The physical properties of a calculus—colour, hardness, smoothness, or roughness, &c.—give little or no clue to its chemical nature. A chemical analysis is always necessary, and this gives valuable indications for after treatment; for instance, in renal calculi, consisting of calcium oxalate, the treatment should be designed to diminish alkalinity, to avoid calcium-rich foods, and to induce the taking of exercise to promote oxidation in the body.

There are, in addition to these common forms of stone, others of a rarer kind, and a list of the different varieties of calculus is as follows—

1. Those composed of uric acid or urates with little or no admixture with phosphates.
2. Mixed calculi, like the preceding, but containing often in alternate layers a large quantity of phosphate.
3. Calcium oxalate calculi, often containing small quantities of phosphates and urates.
4. Phosphatic calculi: a stone composed of pure calcium phosphate is rare; a nucleus of uric acid is generally present.
5. Calcium carbonate calculi are those generally found in the prostate.
6. Cystine calculi are mostly small, smooth, and have a yellow tinge, turning to green on exposure to air. These are rare.
7. Xanthine calculi are still rarer.
8. Fibrinous calculi composed of fibrin or inspissated albumin, have a glassy appearance on fracture; blood calculi have been described in cases of renal hæmaturia; 'urostealith' calculi have been described, and consist of fatty acid with more or less cholesterol. One case of 'indigo' calculus has been described.

No attempt has been made in the foregoing outline sketch of the chemical properties of the urine in health and disease to give any bibliographical references. The literature of urine is enormous, and those interested in it should consult standard works on physiology, physiological chemistry, pathology, and medicine. One of the most trustworthy handbooks on the urine only, and containing abundant references to literature, is Neubauer and Vogel's Analyse des Harns, edited by Huppert, Wiesbaden, C. W. Kreidel. W. D. H.

UROCITRAL, UROPHENIN, *v.* SYNTHETIC DRUGS.

UROPHERIN *v.* SALICYLIC ACID.

UROTROPIN. *Hexamethylenetetramine,* *v.* SYNTHETIC DRUGS.

UROXAMIC ACID, *dicarbaminomalonic acid* $(CO_2H)_2C(NH{\cdot}CO{\cdot}NH_2)_2$ is prepared by the gradual oxidation of uric acid in alkaline solution by the oxygen of the air (Städeler, Annalen, 1851, 78, 286; Strecker, *ibid.* 1870, 155, 177); by oxidising an alkaline solution of uric acid with 5 p.c. potassium permanganate solution (1 atom of oxygen to 1 mol. of uric acid) (Behrend, *ibid.* 1904, 333, 152; Behrend and Schultz, *ibid.* 1909, 365, 21).

Uroxamic acid crystallises in stout prisms or in tetrahedra; it is sparingly soluble in cold water and insoluble in alcohol; it is a strong dibasic acid and its normal alkali salts are neutral towards litmus and phenolphthalein. It readily loses CO_2 and yields allantoic acid when shaken for several days with cold methyl alcohol. When heated with water it breaks down into allanturic acid

$$CO\begin{cases}NH{\cdot}CH(OH)\\ \qquad\quad | \\ NH{\cdot}CO\end{cases}$$

mesoxalic acid and carbamide. The *aniline* and *hydroxylamine* salts are sparingly soluble; the latter melts at 155°; the normal *phenylhydrazine salt* $C_5H_8O_6N_4{\cdot}2C_6H_8N_2$ crystallises in colourless plates, m.p. 130°–132° (decomp.). when boiled with water it is decomposed, yielding the *phenylhydrazine salt* of *mesoxalic acid phenylhydrazone* $C_{15}H_{16}O_4N_4,\frac{1}{2}H_2O$, this forms yellow needles that melt at 154°–158°, solidify at 160° and then decompose at 183°. The normal *silver*, *sodium*, *potassium*, *barium*, *calcium* and *ammonium* salts of uroxamic acid are crystalline. M. A. W.

URUSHIOL *v.* LACQUER.

USNIC ACID $C_{18}H_{16}O_7$ (Stenhouse, Proc. Roy. Soc. 18, 222), $C_{18}H_{18}O_8$ (Paterno, Ber. 9, 345). An acid found in certain lichens (*v.* LICHENS).

UVAROVITE *v.* GARNET.

UVITONIC ACID *v.* BONE OIL.

V

VAL D'ARNO SUPERIORE RESIN *v.* RESINS.

VALENTINITE. Native antimonious oxide Sb_4O_6, *v.* ANTIMONY.

VALERIAN. The root of *Valeriana officinalis* (Linn.) yields on distillation with water an essential oil of a pale yellow or greenish colour, having a strong smell of valerian, an aromatic taste, and acid reaction; sp.gr. 0·90–0·93. Thickens at −15°, and begins to boil at about 200°. Consists of a mixture of valeric acid, a camphene, a stearoptene, and a resin (Pierlot, Ann. Chim. Phys. [iii.] 56, 291; Gerhardt, *ibid.* [iii.] 7, 275).

VALERIC or **PENTOIC ACIDS** C_4H_9COOH. Four isomerides are known.

1. *Valeric acid* $CH_3[CH_2]_3COOH$, is found in pyroligneous acid, and occurs free and as esters in the animal and vegetable kingdoms, chiefly in the roots of *Valeriana officinalis* (Linn.) and of *Archangelica officinalis* (Hoffm.), from which it may be isolated by boiling with water or sodium hydroxide. It may be obtained by boiling *n*-butyl cyanide with potash (Lieben and Rossi, Annalen, 159, 58); by oxidation of α-hydroxycaproic acid (Erlenmeyer, Ber. 1876, 1840); by reduction of lævulic acid (β-acetylpropionic acid) with phosphorus iodide or sodium amalgam (Kehrer and Tollens, Annalen, 206, 233; Fittig and Wolff, *ibid.* 208, 109); by heating propylmalonic acid (Juslin, Ber. 1885, 2504); or by the fermentation of calcium lactate (Fitz, *ibid.* 1880, 1309). A colourless oil having a disagreeable smell, b.p. 186°–186·4° (Fürth, Monatsh. 9, 310); sp.gr. 0·9415 at 20°/4° (Lieben and Rossi); 1 vol. of acid dissolves in 27 vols. of water at 16°.

Methyl valerate boils at 127·3°, and *ethyl valerate* at 144·6° (736·5 mm.).

2. iso*Valeric acid, β-methylbutyric acid*

$CH(CH_3)_2CH_2COOH$.

Discovered in 1817 by Chevreul in dolphin oil from *Delphinus globiceps* and *D. phocæna*, and termed by him *phocenic acid.* Found in other fish oils and in perspiration. In the roots of *Valeriana officinalis* (Linn.), *Archangelica officinalis* (Hoffm.), and in the berries of *Viburnum Opulus* (Linn.). Formed in the putrefaction of albuminoids; by the oxidation of glue, oleic acid, fats, and fusel oil (Lawkrow and Jazukowitsch. J. 1864, 337; Pierre and Pouchet, Ann. Chim. Phys. [iv.] 29, 229). Prepared by the action of alcoholic potash on *iso*propyl cyanide, and by long boiling of amyl alcohol with sodium methoxide (Guerbet, Compt. rend. 128, 512). Colourless oily liquid, smelling like valerian root and putrid cheese; b.p. 173·7° (Kahlbaum, Ber. 1883, 2480), sp.gr. 0·931 at 20°. Soluble in 23·6 parts of water at 20°. The valeric acid of pharmacy is prepared from valerian root or from amyl alcohol. The ammonium and zinc valerates are also used in medicine.

For quantitative estimation of *iso*valeric acid in the presence of acetic acid, *v.* Chapman, Annalen, 1899, 114.

Methyl iso*valerate* boils at 116·7°, and *Ethyl* iso*valerate* at 134·3°.

iso*Amyl* iso*valerate* $C_5H_{11}O(C_5H_9O)$; b.p. 194°; dissolved in spirits of wine is used in confectionery as *essence of apples.*

3. *α-Methylbutyric acid* $CH_3{\cdot}CH(C_2H_5)COOH$ is found in the oil of *Archangelica officinalis* (Hoffm.) (Ciamician and Silber, Ber. 1896, 1815), and may be obtained by heating methyl crotonic acid (tiglic acid) with hydriodic acid (Schmidt and Berendes, Annalen, 191, 117); by the action of sodium amalgam on bromomethyl ethyl acetic acid in a sulphuric acid solution (Pagenstecher, *ibid.* 195, 109); and by heating methyl ethyl malonic acid (Conrad and Bischoff, *ibid.* 204, 151). On oxidising optically active amyl alcohol, a mixture of *iso*valeric and α-methylbutyric acids is obtained which can be separated by converting them into their silver salts, silver *iso*valerate being six times less soluble in water than silver α-methylbutyrate (Erlenmeyer and Hell, Annalen, 160, 301; Conrad and Bischoff, *ibid.* 204, 157). A colourless somewhat mobile liquid; b.p. 173°–174°, sp.gr. 0·938 at 20°/20° (Schütz and Marckwald, Ber. 1896, 26).

4. *αα-Dimethylpropionic acid* $(CH_3)_3C{\cdot}COOH$. Obtained by heating trimethyl acetonitrile with strong hydrochloric acid (Butlerow, Annalen, 170, 151; 173, 355); or by the oxidation of pinacolin (Butlerow, *l.c.*; Friedel and Silva, Ber. 6, 146, and 816). Crystallises in the regular system; m.p. 34°–35°, b.p. 163° (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 475), sp.gr. 0·905 at 50°; soluble in 45 parts of water at 20°.

VALERYDIN, VALIDOL, VALISAN, VALYL, *v.* SYNTHETIC DRUGS.

VALINE was the name given by Fischer (Ber. 1906, 29, 2320) to *α-amino*iso*valeric acid* $CHMe_2{\cdot}CH(NH_2)COOH$. It was isolated first by Gorup-Besanez (Annalen, 1856, 98, 1) from the pancreas of the ox, and occurs in the young seedlings of *Lupinus luteus* (L.), *Lupinus albus* (L.), *Lupinus angustifolius* (L.), *Vicia sativa* (L.), the etiolated seedlings containing more than the green plants (Schulze and Barbieri, J. pr. Chem. 1883, [i.] 27, 337; Schulze and Winterstein, Zeitsch. physiol. Chem. 1902, 35, 308; Schulze, *ibid.* 1894, 20, 306; 1896, 22, 423; Schulze and Castoro, *ibid.* 1903, 38, 199; Wassilieff, Landw. Versuchsstat. 1901, 55, 45; Schulze, Zeitsch. physiol. Chem. 1893, 17, 193; Menozzi, Ber. 1888, 21, 619); it has been found also in Emmenthaler cheese (Winterstein, Zeitsch. physiol. Chem. 1904, 41, 500). Valine is one of the products of hydrolysis of a large number of proteins, such as horn, keratin, edestin, etc., and occurs together with leucine and proline in the fraction of esters, b.p. 60°–90°/10 mm.; it is formed during the process of autolysis of the pancreas and liver, and in peptic and tryptic digestion (Fischer and Dörpinghaus, *ibid.* 1902, 36, 462; Abderhalden and Voitinovici, *ibid.* 1907, 52, 348; Levene and van Slyke, J. Biol. Chem. 1909, 6, 419; Levene, Zeitsch. physiol. Chem. 1904, 41, 393; Lawrow, *ibid.* 1901, 33, 312). The valine occurring naturally is the dextrorotatory form; the racemic form was prepared first synthetically by Fittig and

Clark (Annalen, 1866, 139, 200) by the action of concentrated ammonia on α-bromo*iso*valeric acid at 100°; and later by Lipp (*ibid.* 1880, 205, 1) by hydrolysing the amino*iso*valeronitrile obtained by the condensation of *iso*butaldehyde with ammonia and hydrocyanic acid. It is prepared most conveniently, and the yield is 70 p.c. of the theoretical, by Slimmer's modification of Fittig and Clark's method (Ber. 1902, 35, 400); 500 grms. of α-bromo*iso*valeric acid with 1590 grms. of aqueous ammonia saturated at 15° and 500 grms. of powdered ammonium carbonate are heated in an autoclave at 100° for eight hours; the resulting brownish liquid is filtered and evaporated to one-third its bulk, when most of the amino acid crystallises out. The rest is obtained in the form of its hydrochloride by acidifying the mother liquor with hydrochloric acid, evaporating to dryness and extracting the residue with 80 p.c. alcohol.

Racemic valine can be resolved into its optically active isomerides by the fractional crystallisation of the brucine salt of the formyl derivative; the brucine salt of formyl-*l*-valine being less readily soluble in methyl alcohol than is the corresponding salt of formyl-*d*-valine: *d*-valine and *l*-valine are obtained by hydrolysing with hydrobromic acid the corresponding formyl derivatives (Fischer, Matsubara and Hilpert, Ber. 1906, 39, 2320).

***d,l*-Valine.** In addition to the synthetic methods already described for the preparation of *d,l*-valine, it can be obtained by racemising the active acids by heating them with baryta water at 180° (Fischer, Zeitsch. physiol. Chem. 1911, 33, 162).

d,l-Valine crystallises in colourless plates from alcohol, has a sweet taste, and melts in a closed tube at 298° (corr.) with decomposition; it is readily soluble in water, 1 part dissolving in 11·7 parts of water at 15°, is almost insoluble in cold alcohol or ether, sparingly so in boiling alcohol (Slimmer, *l.c.*); when oxidised by hydrogen peroxide it yields *iso*butaldehyde, *iso*butyric acid (part of which is further oxidised to acetone and carbon dioxide), ammonia and carbon dioxide; with lead peroxide or sodium hypochlorite as the oxidising agent, *iso*butaldehyde is the product (Dakin, J. Biol. Chem. 1908, 4, 63; Langheld, Ber. 1909, 42, 2360). When *dl*-valine undergoes putrefactive decomposition it yields *iso*valeric acid and a small quantity of butylamine; the residual aminovaleric acid is laevorotatory indicating an asymmetric attack by the bacteria (Neuberg and Karczag, Biochem. Zeitsch. 1908, 18, 435).

Salts and derivatives of d,l-*Valine.* The *copper salt* $(C_5H_{10}O_2N)_2Cu$, blue crystals soluble in 3644 parts of methyl alcohol at 20°, or in 9230 parts of 96 p.c. ethyl alcohol at 21°, and sparingly soluble in cold water (Ehrlich and Wendel, Biochem. Zeitsch. 1908, 8, 399); the *silver sal* $C_5H_{10}NO_2Ag$ is crystalline and insoluble in cold water; the *hydrochloride*

$$C_5H_{11}O_2N,HCl,$$

crystalline plates, readily soluble in water or in alcohol, insoluble in ether; the *nitrate*

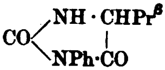
$$C_5H_{11}O_2N,HNO_3$$

is a readily soluble crystalline mass. The *ethyl ester* $CHMe_2{\cdot}CH(NH_2)CO_2Et$ has b.p. 3·5°/8 mm. or 174° with decomposition under atmospheric pressure, sp.gr. 0·9617 at 15°/4°; it forms a sparingly soluble crystalline *picrate*, m.p. 139·5° (corr.), and a soluble *hydrogen* tartrate which on crystallisation suffers partial resolution into its optically active isomerides (Slimmer, *l.c.*). Of the *acyl* derivatives of *d,l*-valine, the *formyl* derivative

$$CHMe_2{\cdot}CH(COOH)NH{\cdot}CHO$$

obtained by heating *d,l*-valine with 1½ times its weight of formic acid crystallises in large rhombic plates from water, sinters at 137° and melts at 140°–145° (corr.), is readily soluble in hot water, alcohol or acetone (Fischer, Ber. 1906, 39, 2322); the *benzoyl* derivative

$$CHMe_2{\cdot}CH(CO_2H)NH{\cdot}CO{\cdot}C_6H_5$$

crystallises in plates, m.p. 132·5° (corr.), is readily soluble in alcohol or ether, sparingly so in water (Slimmer, *l.c.*); the *phenylisocyanate* derivative $CHMe_2{\cdot}CH(CO_2H)NH{\cdot}CO{\cdot}NHPh$ forms colourless plates, soluble in 130 parts of hot water, m.p. 163·5° (corr.) with decomposition, is readily soluble in hot alcohol, sparingly so in ether, and is converted into *phenylisopropylhydantoin*  $\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH\cdot CHPr^{\beta}}\\ \qquad\quad |\\ \mathrm{NPh\cdot CO}\end{array}$ by boiling with hydrochloric acid; this compound crystallises in long needles from ether, m.p. 124°–125° (corr.), and is sparingly soluble in hot water, readily so in alcohol or ether (Slimmer, *l.c.*); the *carbamino* derivative

$$CHMe_2{\cdot}CH(CO_2H)NH{\cdot}CO{\cdot}NH_2,$$

crystallises in needles, m.p. 176°, is soluble in 213 parts of water at 20°, and forms crystalline *barium, mercury* and *silver* salts (Lippich, Ber. 1908, 41, 2962); the *picryl* derivative

$$CHMe_2{\cdot}CH(CO_2H)NH{\cdot}C_6H_2(NO_2)_3$$

forms bright yellow needles, sparingly soluble in cold water, and has m.p. 171° (Hirayama, Zeitsch. physiol. Chem. 1909, 59, 290). *d,l-Valinamide* $CHMe_2{\cdot}CH(NH_2)CONH_2$, obtained by the action of liquid ammonia on the ester prolonged over a period of three months, crystallises from benzene in colourless prisms, m.p. 78°–80° (corr.), and yields a *β-naphthalenesulphonic derivative* $C_{15}H_{18}O_3N_2S$, m.p. 256°–257° (corr.), a *carbethoxy derivative* $C_8H_{16}O_3N_2$, m.p. 143°–144° (corr.) (Königs and Mylo, Ber. 1908, 41, 4427); and a *hydrochloride*

$$CHMe_2{\cdot}CH(CO{\cdot}NH_2)NH_2{\cdot}HCl$$

crystallising in the monoclinic system, and forming a crystalline *platinochloride*

$$(C_5H_{13}ON_2)_2PtCl_6,H_2O$$

(Lipp, Annalen, 1880, 205, 1). d,l-*Valine anhydride* $C_{10}H_{18}O_2N_2$, obtained by heating *d,l*-valine, or by heating the ethyl ester under pressure at 180°–190°, forms long colourless needles, m.p. 303° (corr.) (Fischer and Schenkel, Annalen, 1907, 354, 1).

***d*-Valine** is most conveniently obtained from the two to three weeks old etiolated seedlings of *Lupinus luteus* and *Lupinus albus*, contamination with leucine, which is very difficult to separate from valine, can be obviated by removing the cotyledons from the young plants before they are dried (Schulze and Winterstein, Zeitsch. physiol. Chem. 1902, 35, 312). *d*-Valine is prepared from the synthetic compound by the fractional crystallisation of the brucine salts of the formyl derivative (Fischer, Matsubara and Hilpert, Ber. 1906, 29, 2320).

d-Valine crystallises in colourless, shining six-sided plates. It melts in a closed capillary tube at 315° (corr.); when heated in an open tube it sublimes and decomposes partially with formation of the anhydride. It dissolves in 11 parts of water at 16·5°. The taste is first slightly sweet, then bitter (Fischer, Matsubara and Hilpert, *l.c.*). The natural compound obtained from *Lupinus luteus* has $[\alpha]_D^{16}+28{\cdot}2°$ in 20 p.c. hydrochloric acid (0·5 grm. in 10 c.c.); from *Lupinus albus* $[\alpha]_D^{16}+27{\cdot}9$ in 20 p.c. hydrochloric acid (0·5012 grm. in 10 c.c.) (Schulze and Winterstein, Zeitsch. physiol. Chem. 1902, 35, 299). The synthetic compound prepared by hydrolysing the formyl derivative has $[\alpha]_D^{20}$ $+28{\cdot}75$ in 20 p.c. hydrochloric acid, or $[\alpha]_D^{20}$ $+6{\cdot}42$ in aqueous solution (Fischer, Matsubara and Hilpert, *l.c.*).

Salts and derivatives of d-*valine*. The *copper salt* $(C_5H_{10}O_2N)_2Cu$, blue crystalline plates, soluble in 52 parts of methyl alcohol at 18°. The *hydrochloride* $C_5H_{11}O_2N{\cdot}HCl$, small prismatic crystals readily soluble in water or alcohol, the *platinichloride* is also readily soluble (Schulze and Barbieri, J. pr. Chem. 1883, 27, 337); the *picrolonate* has m.p. 170°–180°, and $[\alpha]_D^{20}+23{\cdot}4$ (Levene and van Slyke, J. Biol. Chem. 1912, 12, 127).

Formyl d-*valine*

$CHMe_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}CHO$

obtained by the resolution of *dl*-formyl valine through the brucine salt, forms small prisms, sinters at 150° and melts at 156° (corr.), and has $[\alpha]_D^{20}+12{\cdot}8°$ to 13·27° in alcoholic solution; d-*valine phenylcarbimide*

$CHMe_2{\cdot}CH(CO_2H)NH{\cdot}CO{\cdot}NHPh$,

forms small microscopic prisms, m.p. 147° (corr.) with decomposition (Fischer, Matsubara and Hilpert, *l.c.*), m.p. 154° (Schulze and Winterstein, Zeitsch. physiol. Chem. 1902, 35, 303), and yields the d-*phenyl*iso*propylhydantoin*

$C_{12}H_{14}O_2N_2$

on treatment with concentrated hydrochloric acid. This forms colourless thin prisms, m.p. 131°–133° (corr.), and has $[\alpha]_D^{20}-97{\cdot}5°$ in alcoholic solution (Fischer, Matsubara and Hilpert, *l.c.*); m.p. 124° (Schulze and Winterstein, *l.c.*); *chloroacetyl*-d-*valine*

$CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CHPr^{\beta}{\cdot}CO_2H$

has m.p. 113°–115° (corr.) $[\alpha]_D^{20}+15{\cdot}8$; *glycyl*-d-*valine* $NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CHPr^{\beta}{\cdot}CO_2H$ has m.p. 254° (corr.), $[\alpha]_D^{20}-19{\cdot}7°$ in aqueous, $-10{\cdot}5°$ in hydrochloric acid or $-6{\cdot}9°$ in sodium hydroxide solution; it forms a crystalline *hydrochloride* and a *copper* salt. The *hydrochloride* of the *methyl ester* $C_8H_{16}O_3N_2{\cdot}HCl$ is converted by methyl alcoholic ammonia into *glycyl*-d-*valinanhydride* $CH_2<\substack{NH{\cdot}CO\\ CO{\cdot}NH}>CHPr^{\beta}$, m.p. 266° (corr.), $[\alpha]_D^{20}+20{\cdot}8°$ in glacial acetic, $+32{\cdot}7°$ in aqueous or $+41°$ in alcoholic solution; l-*valyl*-d-*valine* $C_{10}H_{20}O_3N_2,1\frac{1}{2}H_2O$ becomes anhydrous at 95°/12–15 mm. over phosphoric oxide; has m.p. 308° (corr.), and $[\alpha]_D^{20}-70{\cdot}6°$ to $-74°$; the *hydrochloride* of the *methyl ester* yields on treatment with methyl alcoholic ammonia the *trans-valine-anhydride* $CHPr^{\beta}<\substack{NH{\cdot}CO\\ CO{\cdot}NH}>CHPr^{\beta}$ prisms, m.p. 316°–318° (corr.), which is optically inactive (Fischer and Scheibler, Annalen, 1908, 363, 136).

l-**Valine** is obtained by the resolution of the racemic formyl derivative through the brucine salt (Fischer, Matsubara and Hilpert, *l.c.*); by the action of ammonia on *d*-α-bromo*iso*valeric acid (Fischer and Scheibler, Ber. 1908, 41, 2891); and by the selective action of yeast on *dl*-valine (Ehrlich, Biochem. Zeitsch. 1906, 1, 8; 1908, 8, 438).

l-Valine is soluble in 17·1 parts of water at 25°, possesses a markedly sweet taste, and has $[\alpha]_D^{20}-6{\cdot}06°$ in 6·24 p.c. aqueous solution; $-29{\cdot}04°$ in 20 p.c. hydrochloric acid solution (Fischer, Matsubara and Hilpert, *l.c.*). A specimen obtained from yeast had $[\alpha]_D^{20}-27{\cdot}62°$ in a 4·61 p.c. solution of 20 p.c. hydrochloric acid.

l-*Formylvaline* $CHMe_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}CHO$ crystallises in small prisms, sinters at 150° and melts at 156° (corr.); it has $[\alpha]_D^{20}-12{\cdot}93°$ to 13·07° in alcoholic solution, or $+16{\cdot}9°$ in aqueous solution; l-*valine phenyl*iso*cyanate* $C_{12}H_{16}O_3N_2$ has m.p. 147° (corr.) decomp., and $[\alpha]_D^{20}-19{\cdot}02°$ in absolute alcoholic solution, and yields l-*phenyl*iso*propylhydantoin* $C_{12}H_{14}O_2N_2$ on treatment with hydrochloric acid. It has m.p. 131°–133° (corr.) and $[\alpha]_D^{20}+97{\cdot}22°$ in absolute alcoholic solution. M. A. W.

VALONIA (*Valonée*, Fr.; *Valonea, Ackerdoppen, Orientalische Knoppern*, Ger.). An important tanning material. Is the acorn cup of certain species of oak, usually *Quercus Aegilops* (Linn.), and probably *Q. macrolepsis, Q. graeca, Q. Ungeri*, and *Q. coccifera* (Linn.). The former is most prolific in the highlands of Morea, Roumelia, Greek Archipelago, Asia Minor, and Palestine, whereas the *Q. macrolepsis* forms great forests in Greece. These acorn cups have a diameter up to about 1½ ins., and in good condition possess a bright colour.

The fruit ripens in Asia Minor about July or August, and the trees are then shaken, and the material left on the ground to dry; this is subsequently collected into heaps, and allowed to ferment for some weeks, until the acorn contracts and falls from the cup. The acorn, which contains but little tannin, is employed for feeding purposes.

In Greece distinct qualities of valonia are known, the best (*chamada*) collected about April before the fruit is ripe, a second (*rhabdisto*) in September or October, and a third little used inferior variety (*charcala*).

Smyrna valonia may contain 40 p.c., Greek 19–30, and Candia valonia 41 p.c. of tannin matter, which consists of a mixture of a gallotannin and an ellagitannin. Valonia is, indeed, an excellent source for the preparation of ellagic acid, because it so readily yields a product easy to purify. Extract of valonia frequently undergoes fermentation with deposition of ellagic acid, and to avoid this the employment of antiseptics is to be recommended.

Valonia is especially suited for the manufacture of sole leather, and together with gambier and other materials for dressing leather, but is little employed for dyeing purposes (*cf.* Procter, Principles of Leather Manufacture, 259). A. G. P.

VANADINITE. A mineral consisting of lead chloro-vanadate $(PbCl)Pb_4(VO_4)_3$ crystallised in the hexagonal system and isomorphous with apatite and pyromorphite (*qq.v.*). The formula requires 19·4 p.c. V_2O_5, but this is often partly replaced by phosphoric and arsenic oxides; and the variety *endlichite* forms a passage to the species mimetite (lead chloro-arsenate). The mineral forms small hexagonal prisms usually terminated simply by the basal plane; at times the crystals are curved and barrel-shaped. Globular, warty, and cauliflower-like masses also occur. The colour is usually yellowish or brownish, but crystals from Arizona are bright scarlet. Sp.gr. 6·6–7·2. When touched with a drop of nitric acid a yellow coating of vanadic oxide is formed on the crystals; this affords an easy test for recognising the mineral.

Vanadinite is a mineral of secondary origin in the upper portions of lodes of lead ore, and it sometimes occurs in association with gold. It was formerly found in some quantity at Wanlockhead in Dumfriesshire and near Klagenfurt in Carinthia; and now abundantly in several of the mining districts of Arizona and New Mexico. Recently, it has been met with at Broken Hill in North-Western Rhodesia. Important localities in Arizona are the Red Cloud mine in Yuma Co., the Mammoth gold mine in Pinal Co., the Globe district in Gila Co., and in Pima Co. and Yavapai Co., &c. In New Mexico at the Sierra de los Caballos near Lake Valley in Sierra Co., Magdalena in Socorro Co., Georgetown in Grant Co., &c.

In New Mexico and Arizona the mineral is mined as a source of vanadium. The concentrate containing the vanadinite, together with descloizite, is treated in lead-lined vats with dilute sulphuric acid heated by steam, and the vanadium so obtained in solution as sulphate, the lead remaining in the insoluble residue. The solution is decanted and evaporated, and the vanadium salt ignited to give vanadic oxide. The bulk of this product appears to be used in the manufacture of vanadium-steel, and to a limited extent also as a pigment. Other minerals that have been worked for vanadium are carnotite, descloizite, patronite, and roscoelite (*qq.v.*). L. J. S.

VANADIUM. Sym. V. At.wt. 51·0. This element was discovered by Del Rio (Gilbert's Ann. 1801, 71, 7) in a lead ore, *vanadinite*, from Zimapan in Mexico; the discovery was confirmed by Sefström (Pogg. Ann. 1830, 21, 48), and by Wöhler and Berzelius (*ibid.* 1831, 22, 1; *cf.* Collet-Descotils, Ann. Chim. Phys. 1805, [i.] 53, 260). Upon the work of Berzelius was based the view that vanadium was allied to chromium and molybdenum and, like them, yielded an acidic trioxide, and this idea was current till Roscoe, in 1867, showed that the substance believed to be the metal in earlier investigations had been either an oxide or a nitride, and that the compounds of vanadium in general showed that the elements belonged to the phosphorus group.

Occurrence. Minerals containing a large proportion of vanadium are rare, but the metal is very widely distributed in small quantities. Vanadium occurs as vanadic acid in *vanadinite* with the native copper of Lake Superior, and in *alaite* (Nenadkevitsch, Bull. Acad. Sci. St. Petersbourg, 1909, 185); as lead vanadate, with lead chloride, in *vanadinite*; as lead pyrovanadate as *descloizite*; as hydrated vanadate of lead and copper in *mottramite* and *psittacinite*; as vanadate of copper in *turanite* (Nenadkevitsch, *l.c.*); as lead vanadate containing zinc and manganese in *dechenite*, *aroxene*, and *eusynchite*; as vanadate of lead and arsenic in *endlichite*; as bismuth vanadate in *pucherite*; as the basic oxide V_2O_3 in the vanadium muscovite *roscoelite* (Hillebrand, Turner and Clarke, Amer. J. Sci. 1899. [iv.] 7, 451); as vanadate of copper, barium, and calcium in *volborthite*; and as vanadium sulphide V_2S_5 with sulphur, in *patronite* (Hillebrand, *ibid.* 1907, [iv.] 24, 141; Hewett, Eng. & Min. J. 1906, 82, 385; Trans. Amer. Inst. Min. Eng. 1910, 40).

Vanadium is present in magnetites and in most other iron ores (Pope, Chem. Soc. Abstr. 1900, ii. 409), and becomes concentrated in the residues from their treatment, especially by the Thomas-Gilchrist process. It is said to be diffused, with titanium, through all primitive granite rocks (Dieulafait; Hillebrand, Amer. J. Sci. 1898, 6, 209; 7, 294), and has been found by Deville in *bauxite*, *rutile*, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands. Jorissen has found vanadium in the coal of Liége (Bull. Accad. Roy. Belg. 1905. 178). Scacchi has observed its presence in incrustations on the Vesuvian lava of 1631, and Donath has found as much as 0·16 p.c. of vanadic acid in a sample of commercial caustic soda (Dingl. poly. J. 240, 318). It occurs in the sun and has been found in stony meteorites (Hasselberg, Vetensk. Akad. Svenska. 1899, 56, 131).

Extraction.—Ammonium metavanadate was formerly prepared on a commercial scale by the Magnesium Metal Co. at Patricroft near Manchester.

The mineral employed was *mottramite* $(PbCu)_3(VO_4)_2.2PbCu(HO)_2$, which occurs in the copper-bearing Keuper beds at Alderley Edge and Mottram St. Andrew's, in Cheshire, as a film on the grains of standstone. The sand is digested in concentrated hydrochloric acid, and the acid liquid is withdrawn. The solution, with the washings of the residue, is concentrated and evaporated with an excess of ammonium chloride, forming ammonium metavanadate, which, being insoluble in a concentrated solution of ammonium chloride, is precipitated. After being freed from copper and iron by repeated crystallisation, it is gently roasted in a porcelain vessel, with production of vanadium pentoxide. This is suspended in water and subjected to a current of ammonia gas, with formation of ammonium metavanadate, the solution being separated from the silica, phosphates, &c., which are not affected by ammonia, crystallised until free from phosphates, and gently ignited to produce pure vanadium pentoxide (*v.* Roscoe, Phil. Trans. 1867, 158, 1

The greater part of the vanadium of commerce is now extracted from the vanadinite of Spain, Chile, and the Argentine. The mineral is fused with potassium nitrate, alone or mixed with sodium carbonate, the mass is lixiviated, and the solution acidified, or, better, evaporated with ammonium chloride in order to precipitate alumina and silica. From the clear solution barium chloride and ammonia precipitate the barium salts of vanadic, chromic, and molybdic acids, &c., and on treating the product with sulphuric acid, followed by ammonia and water, the vanadium goes into solution as ammonium metavanadate, which is finally precipitated by the addition of ammonium chloride. Vanadic acid may also be separated from mixtures of sodium vanadate and silicate by the addition of more vanadic acid. This precipitates the silica and leaves only fairly pure sodium vanadate in solution (Herrenschmidt, Compt. rend. 1904, 139, 862).

According to Witz and Osmond (Bull. Soc. chim. 1882, [ii.] 38, 49; Compt. rend. 95, 42), the slags produced while working the Thomas-Gilchrist process at the Creusot ironworks contain nearly 1·5 p.c. of vanadium, the quantity of that metal thus concentrated amounting to 60,000 kilos (nearly 59 tons) annually. They recommend the following process for the separation: 1 kilo of the roughly broken slag is treated with a quantity of hydrochloric acid insufficient to attack the whole (about 1 litre of acid of 21°–22°Bé.) without stirring, 3 litres of water being added, and the whole remaining at rest for 2 days. The solution, having a sp.gr. of about 27°Bé. at 36°, is decanted and diluted to 15°Bé., and the silica is removed. The solution contains the vanadium in the hypovanadic condition, and may be used at once for the production of aniline black. If it is desired to produce hypovanadic phosphate, the solution is nearly neutralised and about 250 c.c. of saturated ammonium acetate solution is added. The bluish-grey precipitate produced, containing phosphates of iron, aluminium, and vanadium, is re-dissolved and again treated with ammonium acetate, the precipitate containing about 20 p.c. of vanadium.

If the slag contains less than 1·5 p.c. of vanadium, the hydrochloric acid solution is neutralised by the addition of a further quantity of finely-powdered slag. The solution becomes colourless, and a greyish granular precipitate separates, containing the whole of the vanadium and smaller proportions of the other less soluble phosphates. The precipitate is re-dissolved and re-precipitated as before. For the preparation of ammonium metavanadate, the phosphatic precipitate is roasted at incipient redness, and the ochreous-yellow mass of impure pentoxide is dissolved with the aid of ammonia, boiled until colourless and filtered, the ammonium metavanadate being precipitated by the addition of excess of ammonium chloride. From 4 kilos. of slag containing 1·5 p.c. of vanadium, about 250 grms. of ammonium metavanadate may be produced. It is a colourless transparent salt, or white powder, difficultly soluble in water, insoluble in a concentrated solution of ammonium chloride and in ether. It was formerly used, in conjunction with sodium chlorate, as an oxygen-carrier in the formation of the finest aniline black, only an extremely small quantity of the salt being required for a large amount of aniline.

Später attempted (1896) to employ the ash of an anthracite from Yauli (Peru) containing 28 p.c. of vanadium, but was unsuccessful.

From minerals in which it occurs with uranium, vanadium may be extracted by fusing with potassium hydrogen sulphate, lixiviating the mass and concentrating the solution thus obtained. The solution is reduced with zinc and the vanadium precipitated with ammonia and ammonium carbonate (Gin, Elektrochem. Zeit. 1906, 13, 119).

Haynes states (Mines and Minerals, 1909, 30, 139) that vanadium is extracted from *carnotite*, in West Colorado, by dissolving out the uranium and vanadium with hot sodium carbonate solution, precipitating the uranium with caustic soda, and throwing down the vanadium from the mother liquor as calcium vanadate.

Fleck and Haldane recommend that the crushed ore be treated with 15–20 p.c. sulphuric acid, the acid liquid neutralised by the addition of fresh ore, and the clear solution fractionally precipitated with limestone, whereby a complex mixture, rich in vanadium, is obtained, from which the element may be extracted by any ordinary method (U. S. Pat. 880752).

Preparation of metallic vanadium. Roscoe has given two methods for the preparation of the metal: (*a*) the reduction of vanadium nitride in hydrogen, which never gives a pure product; and (*b*) the reduction of anhydrous, oxygen-free vanadium dichloride in dry hydrogen. For a long time the latter method was the only one known by which the pure metal could be obtained (*v.* Roscoe and Schorlemmer, Treatise on Chemistry), but it can also be prepared by the reduction of vanadium pentoxide with 'mischmetall,' a mixture of alkaline earth metals extracted from the residues from the manufacture of thoria (Weiss and Aichel, Annalen, 1904, 337, 380). The mixture of mischmetall and pentoxide is placed in a magnesia crucible and fired; the heat of reaction is sufficient to melt the reduced metal, which is afterwards found as a compact mass in the crucible (Muthmann, Weiss and Riedelbauch, *ibid.* 1907, 355, 58).

It was formerly supposed that Goldschmidt's aluminium reduction method would not give pure vanadium from the pentoxide (Koppel and Kaufmann, Zeitsch. anorg. Chem. 1905, 45, 352), but under certain conditions Vogel and Tammann have, by this method, obtained a regulus containing 99 p.c. vanadium, with a little silicon and aluminium (*ibid.* 1909, 64, 225).

Reduction of the oxide with metallic calcium, according to Muthmann's method, gives a product containing only 91–93 p.c. of vanadium. A purer regulus is obtained by reducing with a mixture of calcium and aluminium (Prandtl and Bleyer, *ibid.* 1909, 64, 217).

Vanadium produced by the reduction of the pentoxide in the electric furnace contains 10–25 p.c. of carbon and consists chiefly of vanadium carbide. A product containing less carbon can be obtained by conducting the operation in an atmosphere of hydrogen (Moissan, Compt. rend. 116, 1225; 122, 1297; Zeitsch. anorg. Chem. 14, 174).

The pure metal can also be obtained by the electrolysis of a solution of sodium vanadate in hydrochloric acid, using carbon electrodes and a current density of 0·018–0·020 amp. per sq. cm., and maintaining the temperature about 80° (Cowper-Coles, Eng. and Min. J. 67, 744; von Bolton, Zeitsch. Elektrochem. 1905, 11, 45).

Properties.—Pure vanadium is a silver-white metal, similar in appearance to cast iron, and crystallises in hexagonal rhombohedra, like the other elements of its group. Its hardness is 7·5 on Mohr's scale, and it is as brittle as glass. It has sp.gr. 6·025 at 15°/15° (sp.gr. 5·5 at 15°/15°, Roscoe), and its specific heat is 0·124 (Matignon and Monnet, Compt. rend. 134, 542; Muthmann, Weiss and Riedelbauch, *l.c.*), which, assuming the atomic heat to be 6·4, confirms the atomic weight of 51.

The melting-point is very high, but the data given by various investigators are not in agreement. Werner von Bolton, using the photometric method of Lummer, found it to be 1680°. Vogel and Tammann give it as 1750°, ±30° (Zeitsch. anorg. Chem. 1908, 58, 73).

It is stable in moist or dry air at ordinary temperatures, and a polished surface retains its lustre for weeks. It is unacted upon by bromine water, aqueous alkali solutions, hydrochloric acid, or cold sulphuric acid. It is dissolved by hydrofluoric acid or hot sulphuric acid forming green solutions, and is attacked by nitric acid or *aqua-regia.* Molten potash or saltpetre rapidly dissolve the metal with formation of an alkali vanadate. Metallic vanadium reduces solutions of mercuric chloride and bromide, cupric chloride and bromide, and ferric chloride to the lower haloid salts, and it precipitates the metal from solutions of auric chloride, silver nitrate, platinic chloride, iridium tetrachloride, &c.

Alloys of vanadium can be prepared in the electric furnace by the reduction of the pentoxide in presence of a second metal or its oxide (Moissan, Compt. rend. 1896, 122, 1297). The chief industrial use of vanadium is in the preparation of special steels, which are largely used for motor-car work; it is introduced into the molten steel as *ferro-vanadium*, an alloy prepared by electric-furnace methods. The addition of 0·1–0·25 p.c. of vanadium to chromium, manganese, or other open-hearth or crucible steels greatly increases the elastic limit and the ultimate tensile stress without reducing the ductility (J. Kent Smith, J. Soc. Chem. Ind. 1906, 291; *cf.* Auchy, J. Ind. and Eng. Chem. 1909, 1, 455).

Colloidal solutions of vanadium have been prepared by Svedberg (Ber. 1906, 39, 1712).

OXIDES OF VANADIUM.

There are five oxides of vanadium, analogous to the oxides of nitrogen—

Vanadium suboxide, V_2O;
„ monoxide, hypovanadious oxide, V_2O_2;
„ sesquioxide or trioxide, V_2O_3;
„ dioxide, hypovanadic oxide, $V_2O_4(VO_2)$;
„ pentoxide, vanadic anhydride, V_2O_5

The first three of these act as basic oxides, forming salts with acids; the last two behave both as weak basic oxides and acid-forming oxides.

Vanadium suboxide V_2O is obtained as a brown powder by the exposure of finely divided metallic vanadium to the air. No salts of this oxide have been prepared.

Vanadium monoxide V_2O_2 or VO (*vanadyl*) is obtained as a lustrous grey solid by reducing the higher oxides with metallic potassium, or by passing the vapour of vanadyl trichloride with hydrogen over red-hot carbon. It has sp.gr. 3·64, is brittle and conducts electricity. At a red heat it burns in air to form the trioxide, and it combines directly with chlorine to form the oxytrichloride. This oxide was supposed by Berzelius to be the metal.

Vanadium monoxide dissolves in acids to form the corresponding salts, which have a violet colour and act as powerful reducing agents. The solution in hydrochloric acid has been suggested as a reagent for the removal of arsenic from hydrochloric acid gas in the process of manufacture, the arsenic being reduced to the free state and remaining suspended in the liquid (D. R. P. 164355).

Vanadium trioxide V_2O_3, obtained by reducing the pentoxide with hydrogen or carbon at a red heat, is a black powder of sp.gr. 4·7. In air it oxidises, slowly at the ordinary temperature, quickly when heated, forming the dioxide V_2O_4. It is insoluble in most acids.

Vanadium dioxide V_2O_4 or VO_2 is prepared by the oxidation of the trioxide or by the partial reduction of the pentoxide. It is a steel-coloured powder composed of dark indigo-coloured crystals. It dissolves in acids to form solutions of vanadyl salts of a bright blue colour, and in alkalis to form *vanadites* (*v.i.*). A *hydrate*, $V_2O_4,7H_2O$, or $V_2O_2(OH)_4,5H_2O$, is obtained as a greyish-white precipitate by adding sodium carbonate to a solution of a vanadyl salt. At 100° it loses 4 molecules of water, forming $V_2O_4,3H_2O$.

Hypovanadic acid (*vanadious acid*) $H_4V_2O_6$ has been prepared by boiling a solution of the dioxide VO_2, in aqueous sulphurous acid. It is a pink crystalline powder (Gain, Compt. rend. 1906, 143, 823; *see* also *ibid.* 1154), and can exist in a green isomeric form (Gain, *ibid.* 1907, 146, 403; Ann. Chim. Phys. 1908, [viii.] 14, 224).

The salts in which VO_2 is the acidic oxide are derived from the partial anhydrides $H_2V_2O_5$ and $H_2V_4O_9$.

Potassium and *sodium vanadites*

$K_2V_4O_9,4H_2O$ and $Na_2V_4O_9,4H_2O$

are prepared by adding excess of caustic alkali to a solution of vanadyl sulphate or chloride (*v.* Koppel and Goldmann, Zeitsch. anorg. Chem. 1903, 36, 281). They form reddish-brown crystalline scales and dissolve in water to dark-brown solutions.

Vanadium pentoxide V_2O_5 is the final product of most commercial processes for the extraction of vanadium from its ores. The pure oxide is best prepared by decomposing vanadyl trichloride with water and fusing the product, or by the decomposition of ammonium metavanadate by heat (Matignon, Chem. Zeit. 1905, 29, 986; *see* also Beard, Ann. Chim. anal. 1905, 10, 41).

Vanadium pentoxide forms large rhombic prisms, of a fine ruby-red colour by transmitted light, of sp.gr. 3·35, soluble in about 1000 parts of water with formation of a yellowish, tasteless solution which reddens litmus. At 658° (Carnelley) it fuses, forming a red liquid, which recrystallises in needles, with incandescence, on cooling.

When prepared by igniting ammonium metavanadate, treating the residue with nitric acid and drying at a gentle heat, it is a yellow, hygroscopic powder which forms hydrates with 1, 2, and 8 molecules of water, and is soluble in water to the extent of 8 parts in 1000. When the oxide is heated at 440°, or fused, two different sparingly soluble modifications are formed (Ditte, Compt. rend. 1885, 101, 698).

Vanadium pentoxide is reduced to V_2O_4 by the action of SO_2, or by evaporation with hydrochloric acid; to V_2O_3 by hydriodic acid, by magnesium and hydrochloric acid, or by hydrogen in the dry way; to V_2O_2 by zinc and hydrochloric acid (Glasmann, Ber. 1905, 38, 600; Chapman, Analyst, 1907, 32, 250).

The pentoxide was formerly used in the preparation of aniline black, and it acts as a carrier of oxygen in many reactions, *e.g.* the electrolytic oxidation of organic compounds in acid solution (Meister, Lucius and Brüning, D. R. P. 172654), and the oxidation of sugar to oxalic acid or of stannous to stannic chloride (Ludwig, Moeser and Lindenbaum, J. pr. Chem. 1907, [ii.] 75, 146; D. R. P. 183022).

The Vanadic Acids and their Salts.

Orthovanadic acid H_3VO_4 has not been prepared.

Metavanadic acid HVO_3 may be obtained by boiling copper metavanadate with aqueous sulphurous acid. A mixture of brown and yellow crystals is first produced, the former being redissolved on continued boiling with excess of sulphurous acid. The remaining yellow crystals consist of metavanadic acid. The acid may also be prepared by addition of a solution of ammonium metavanadate to one of copper sulphate containing excess of ammonium chloride, until a permanent precipitate is produced, and heating for a few hours at 75°. The whole of the vanadium is slowly precipitated, the colour being finer when precipitation is slow (Gerland, Ber. 1876, 9, 874). Metavanadic acid forms brilliant golden or orange-coloured scales, which are used as a pigment in place of gold bronze under the name 'vanadium bronze.'

Pyrovanadic acid $H_4V_2O_7$, prepared by the action of nitric acid on an acid vanadate, is a brown precipitate which when air-dried has the above composition (von Hauer, *v.i.*).

Hexavanadic acid $H_4V_6O_{17}$, formed when a solution of pervanadic acid is allowed to stand, is known only in solution (Düllberg, Zeitsch. physikal. Chem. 1903, 45, 170).

The following sodium vanadates are known, and may be taken as typical of the vanadates in general—

Sodium metavanadate, $NaVO_3$;
„ orthovanadate, Na_3VO_4;
„ pyrovanadate, $Na_4V_2O_7$;
„ tetravanadate, $Na_3HV_4O_{12}$;
„ hexavanadate, $Na_2H_2V_6O_{17}$

(*v.* also von Hauer, J. pr. Chem. 1856, [i.] 69, 385; 1859, 76, 156 and 929; 1860, 80, 324; Carnelley, Chem. Soc. Trans. 1873, 323). In solution the metavanadates are most stable, and the orthovanadates least stable, the pyrovanadates being intermediate. This is the reverse of the order of stability of the phosphates. At high temperatures orthovanadates are the most stable salts, being produced, *e.g.*, by fusing alkali carbonates with vanadium pentoxide. The *alkali pyrovanadates*, prepared by fusing the pentoxide with excess of alkali carbonate and crystallising from water, are soluble, whilst the pyrovanadates of heavy metals are mostly insoluble.

The *alkali metavanadates* are obtained by boiling a solution of alkali carbonate with the pentoxide, and are colourless salts which give yellowish-red anhydro-salts on treatment with acid. The metavanadates of heavier metals are usually yellow. Pure silver metavanadate is precipitated on addition of silver nitrate to a neutral solution of an alkali vanadate (Browning and Palmer, Amer. J. Sci. 1910, 30, 220).

A test which distinguishes between ortho- and meta- vanadates depends on the colour of the copper salts of the acids which are blue-green and light yellow respectively.

A series of double stannates and vanadates of sodium has been described by Prandtl and Rosenthal (Ber. 1907, 40, 2125).

Ammonium metavanadate NH_4VO_3 is the most important salt of vanadic acid. It may be prepared by dissolving vanadium pentoxide in excess of aqueous ammonia and then, by evaporation or by adding alcohol or excess of ammonium chloride, it is thrown out of solution as a white crystalline powder.

A 'vanadium ink' is produced by the addition of gallic acid to a mixture of neutral ammonium metavanadate and gum water. This ink is not destroyed by acids, alkalis, or chlorine, but does not appear to be permanent. Soerensen (J. Soc. Chem. Ind. 1, 185) recommends the use of a solution of 1 lb. neutral ammonium metavanadate in 10 gals. of water for producing a permanent black dye on leather which has been tanned with nut galls.

Pervanadic acid HVO_4, prepared by adding finely powdered vanadium pentoxide to a solution of hydrogen peroxide acidified with sulphuric acid, forms yellow crystals soluble in water, giving a deep-red solution (Werther, J. pr. Chem. 1861, 83, 195; Pissarjewsky, Zeitsch. physikal. Chem. 1903, 43, 173). The *potassium salt* KVO_4 forms a yellow microcrystalline precipitate (*see* also Melikoff and Pissarjewsky, Zeitsch. anorg. Chem. 1899, 19, 405; Pissarjewsky, *ibid.* 1903, 32, 341; Melikoff and Kasanezky, *ibid.* 1901, 28, 242; Melikoff and Jelhchaninoff, Ber. 1909, 42, 2291).

Vanadiselenious acid $3V_2O_5{\cdot}4SeO_2,4H_2O$ and its salts have been described by Prandtl (Ber. 1905, 38, 1305).

SALTS OF VANADIUM.

Vanadium trifluoride $VF_3,3H_2O$ crystallises in dark-green octahedra from a solution of the trioxide in hydrofluoric acid. Addition of potassium fluoride precipitates the *double potassium salt* $2KF{\cdot}VF_3,H_2O$ as a bright green crystalline powder.

Vanadium oxydifluoride VOF_2, from the dioxide and hydrofluoric acid, forms blue prismatic crystals (hydrated).

The pentoxide also dissolves in hydrofluoric acid, but no other fluoride has been isolated. Numerous double fluorides have been described (*see* Petersen, J. pr. Chem. 1889, [ii.] 40, 193, 271; Piccini and Giorgis, Gazz. chim. ital. 1888, 18, 186; Baker, *ibid.* 1878, 388; Costăchescu, Ann. Sci. Univ. Jassy, 1910, 6, 117).

Vanadium tetrachloride VCl_4 is formed by the action of excess of chlorine on the metal or the mononitride. It is prepared by passing the vapour of vanadyl trichloride with chlorine over red-hot sugar charcoal, or by the action of chlorine on the impure metal obtained by Goldschmidt's method (Koppel, Goldmann and Kaufmann, Zeitsch. anorg. Chem. 1905, 45, 345). and is separated from admixed oxychloride by fractional distillation.

It is a deep brown-red, viscous liquid which fumes in air. It boils at 154°, and when heated or exposed to light loses chlorine, forming the trichloride (*v.i.*). It has sp.gr. 1·8584 at 0°, and V.D. 6·69 at 205°. Water decomposes it with formation of a blue solution of vanadyl chloride.

The *pentachloride* does not appear to exist.

Vanadium trichloride VCl_3 is obtained by the decomposition of the tetrachloride, by passing the vapour of the tetrachloride with hydrogen through a red-hot tube, or by heating the trisulphide in chlorine (Halberstadt, Ber. 1882, 15, 1619). It is most easily prepared by passing first the vapour of carbon disulphide and then dry chlorine over heated vanadium pentoxide.

The trichloride thus obtained forms beautiful purple tabular crystals, resembling chromium trichloride. Heated in air, it decomposes yielding the pentoxide. When ignited in hydrogen it does not volatilise, but is reduced to the dichloride. It has sp.gr. 3·0, and is extremely hygroscopic.

The hydrated salt $VCl_3,6H_2O$ is obtained by evaporating *in vacuô* a solution of the trioxide in hydrochloric acid (Locke and Edwards, Amer. Chem. J. 1898, 20, 594), or by reducing electrolytically a solution of the pentoxide in hydrochloric acid and saturating the resulting solution with hydrogen chloride (Piccini and Brizzi, Zeitsch. anorg. Chem. 1899, 19, 394). It is a green crystalline powder, and when heated begins to decompose before all the water has been driven off.

Vanadium dichloride VCl_2 is prepared by reducing the trichloride, by heating to redness a mixture of the tetrachloride and hydrogen, or by heating the silicide VSi_2 in chlorine (Moissan and Holt, Compt. rend. 1902, 135, 78).

It forms deliquescent, apple-green hexagonal plates having a micaceous lustre; it dissolves in water to form a solution which bleaches strongly, and is a more powerful reducing agent even than chromous chloride (Piccini and Marino, Zeitsch. anorg. Chem. 1902, 32, 68).

When the solid is heated in hydrogen the pure metal is obtained (Roscoe).

Vanadyl trichloride $VOCl_3$ (*vanadium oxytrichloride*) is prepared (1) by the action of chlorine on the trioxide, some pentoxide being formed according to the equation

$$3V_2O_3+6Cl_2=4VOCl_3+V_2O_5;$$

(2) by heating a mixture of the pentoxide and carbon in a current of chlorine; (3) by passing dry hydrogen chloride over a mixture of vanadium and phosphorus pentoxides at 60° (Ephraim, Zeitsch. anorg. Chem. 1903, 35, 66).

The product is usually dark-coloured from the presence of the tetrachloride, and is best purified by distillation over metallic sodium in an atmosphere of carbon dioxide.

A solution in acetic acid may be obtained by the action of dry hydrogen chloride on a solution of the pentoxide in glacial acetic acid (Koppel and Kaufmann, *ibid.* 1905, 45, 352).

Pure vanadyl trichloride is a lemon-yellow mobile liquid; b.p. 127·°2, sp.gr. 1·86534 at 0°/4° (Thorpe). In contact with moist air it evolves dense red fumes. Water decomposes it with formation of vanadic and hydrochloric acids, and with a large quantity of water it yields a yellow solution (*see* Agafonoff, J. Russ. Phys. Chem. Soc. 1903, 35, 649). Heated in a current of ammonia it yields the mononitride. At 70° it combines with ether yielding the compound $VCl_3(OC_2H_5)_3$, crystallising in red needles (Bedson, Chem. Soc. Trans. 1876, i. 309), and it forms a compound with pyridine.

Vanadium may be quantitatively volatilised as the trichloride by heating its compounds in a current of carbon tetrachloride vapour (Jannasch and Harwood, J. pr. Chem. 1909, [ii.] 80, 127).

Vanadyl dichloride $VOCl_2$, crystallising in deliquescent green tablets, is formed when the oxytrichloride is heated with zinc at 400°, or with hydrogen at a red heat. The latter method of reduction yields *vanadyl monochloride* $VOCl$, a flocculent brown powder, insoluble in water, and *divanadyl monochloride* V_2O_2Cl, a yellow crystalline powder. Double compounds of $VOCl_2$, with the hydrochlorides of pyridine and quinoline, have been described (Koppel, Goldmann and Kaufmann, Zeitsch. anorg. Chem. 1905, 45, 345).

Divanadyl tetrachloride $V_2O_2Cl_4,5H_2O$ is obtained as a brown, amorphous deliquescent mass by the evaporation of a solution of the pentoxide in hot concentrated hydrochloric acid. It dissolves in water to a blue solution which is turned brown by hydrochloric acid or alcohol, possibly owing to the formation of different hydrates (Crow, Chem. Soc. Trans. 1876, ii. 453).

Another oxychloride $V_2O_3Cl_2,4H_2O$ is obtained by similar methods as a dark-green deliquescent solid (Ditte, Compt. rend. 1886, 102, 1310).

Vanadium tribromide VBr_3 is prepared by the action of dry bromine on the metal or on the mononitride, or a mixture of the trioxide and carbon at a red heat. It is a deliquescent solid which is very unstable and loses bromine even at the ordinary temperature.

The hydrated bromide $VBr_3,6H_2O$ is prepared in a similar manner to the corresponding chloride (*q.v.*).

Vanadyl tribromide $VOBr_3$, prepared by passing bromine vapour over the heated trioxide, is a dark-red liquid, sp.gr. 2·967 at 0°, b.p. 130° under 100 mm. Heated to 180° it suddenly decomposes into free bromine and *vanadyl dibromide* $VOBr_2$, a brownish-yellow powder.

Vanadium triiodide (hydrated) $VI_3,6H_2O$ is prepared in the same manner as the corresponding bromide and iodide.

Divanadyl tetriodide $V_2O_2I_4,8H_2O$ is obtained as a dark-coloured deliquescent solid by the action of hydriodic acid on vanadium pentoxide (Ditte, Compt. rend. 1886, 102, 1310).

Vanadium monosulphide VS, obtained by heating the sesquisulphide in hydrogen, is a brown powder soluble in nitric acid.

Vanadium sesquisulphide (*vanadium trisulphide*) V_2S_3 is prepared by heating the trioxide in a current of hydrogen sulphide or the pentoxide in the vapour of carbon disulphide. It is a greenish-black powder (*see* Kay, Chem. Soc. Trans. 1880, 728).

Vanadium pentasulphide V_2S_5 is obtained as a black powder by heating the trisulphide with sulphur. This sulphide is acidic and gives rise to a series of *thiovanadates*, which are best prepared by passing hydrogen sulphide into cooled solutions of the corresponding vanadates.

Vanadyl sulphite $6VO_2{\cdot}4SO_2,9H_2O$ is obtained as a dark blue crystalline powder by reducing barium vanadate with sulphur dioxide. Gain has described a sulphite $4VO_2{\cdot}3SO_2,10H_2O$, crystallising in silky blue needles (Compt. rend. 1906, 143, 823; *see* also *ibid.* 1907, 144, 1157).

Vanadious sulphate $VSO_4,7H_2O$ is best prepared by acting with sulphur dioxide on a suspension of vanadium pentoxide in sulphuric acid and then reducing the solution electrolytically. On evaporation *in vacuô* the salt is obtained in reddish-violet monoclinic crystals which appear to be isomorphous with ferrous sulphate. The solution of the salt is a powerful reducing agent and bleaches strongly.

Vanadious sulphate forms a series of double salts with the alkali sulphates (*see* Piccini, Zeitsch. anorg. Chem. 1899, 19, 204; Piccini and Marino, *ibid.* 1902, 32, 55; Marino, *ibid.* 1906, 50, 49; Rutter, *ibid.* 1907, 52, 368; and Zeitsch. Elektrochem. 1906, 12, 230).

Vanadium sesquisulphate $V_2(SO_4)_3$, prepared by reducing a solution of vanadium pentoxide in sulphuric acid with magnesium, or by the electrolytic reduction of vanadyl sulphate, forms a green solution from which green crystals of the acid salt $V_2(SO_4)_3,H_2SO_4,12H_2O$ separate out. By dissolving this salt in water, adding sulphuric acid and heating at 180° in a current of carbon dioxide, the sesquisulphate separates out as a yellow crystalline powder, insoluble in water (Stähler and Wirthwein, Ber. 1905, 38, 3978).

Several *vanadium alums* have been prepared.

Vanadyl sulphate $V_2O_2(SO_4)_2$ is prepared (*a*) in the insoluble form by dissolving the dioxide VO_2 in sulphuric acid and heating the solution at 260° (Gerland, Ber. 1877, 10, 2109; Koppel and Behrendt, Zeitsch. anorg. Chem. 1903, 35, 154); (*b*) in the soluble form by heating the insoluble form with water at 130°, or by dissolving the dioxide in sulphuric acid, evaporating, and treating the residue with alcohol. Both forms are blue, and by crystallisation of the soluble form under different conditions hydrates with 13, 10, 7, 4, 3, and 2 molecules of water are obtained.

Strongly acid solutions deposit the acid sulphate $(V_2O_2)H_2(SO_4)_3$, crystallising with 5 molecules of water. When heated it gradually loses water, yielding various lower hydrates, and, finally, at 190°, the *anhydrous salt*

$$2VO_2{\cdot}3SO_3,$$

which forms microscopic green tetragonal crystals, sparingly soluble in water (Koppel and Behrendt, *l.c.*; Gain, Compt. rend. 1906, 143, 1154).

Divanadyl trisulphate $(VO)_2(SO_4)_3$ is obtained in ruby-red octahedra by boiling the pentoxide with excess of sulphuric acid (*see* Ditte, *ibid.* 1886, 102, 757). Other basic salts, *e.g.* $(VO_2)O(SO_4)_2$ and $VO(OH)SO_4$ have been described (*see* Gerland, Ber. 1878, 11, 98).

Vanadium mononitride VN may be obtained by the direct union of its elements or by heating ammonium metavanadate or the pentoxide to whiteness in a current of ammonia. It is a brown powder, oxidised to the blue oxide when heated in air.

Vanadium dinitride VN_2 is a black powder obtained by the action of ammonia on vanadyl trichloride.

Many phosphovanadic and arsenovanadic acids are known, giving rise to numerous derivatives (*see* Ditte, Compt. rend. 1886, 102, 757; Gibbs, Amer. Chem. J. 1886, 7, 118, 209; Friedheim, Ber. 1890, 23, 1530, 2600; Gain, Compt. rend. 1907, 144, 1271; Mawrow, Zeitsch. anorg. Chem. 1907, 55, 147). Blum has described a series of phosphovanadic molybdates (J. Amer. Chem. Soc. 1908, 30, 1858).

Vanadium carbide VC, obtained by heating the pentoxide with carbon in the electric furnace, forms hard crystals of sp.gr. 5·36.

Vanadium silicides. Two silicides are known: V_2Si, sp.gr. 5·48; and VSi_2, sp.gr. 4·42. Both are obtained in the electric furnace from the oxide and silicon. They are hard, crystalline substances, having a metallic lustre (Moissan and Holt, Compt. rend. 1902, 135, 78, 493).

A vanadium aluminium silicide $V_6Al_2Si_{12}$ has been described by Manchot and Fischer (Annalen, 1907, 357, 129).

Detection and estimation of vanadium. Vanadium may be detected *qualitatively* by the behaviour of its compounds on oxidation and reduction, yellow or red solutions of vanadates yielding blue solutions of vanadyl salts on reduction with zinc and acid. Addition of ammonium chloride to a solution of a vanadate precipitates white ammonium metavanadate. The most delicate test known for vanadium consists in adding hydrogen peroxide and ether to a solution of a vanadate acidified with sulphuric acid; a yellow or red colour is produced in the *aqueous* layer (G. Werther, J. pr. Chem. 1863, [i.] 88, 195; Campagne, Chem. Zentr. 1904, [ii.] 1167). Vanadium may also be detected spectroscopically (*see* Purvis, Trans. Camb. Phil. Soc. 1906, 20, 193; Pollok, Sci. Proc. Roy. Dubl. Soc. 1909, 11, 331).

Vanadium is usually estimated volumetrically by oxidation methods after other reducible metals have been eliminated. *See* art. ANALYSIS.

VANADIUM INK *v.* VANADIUM.

VANADIUM MICA *v.* ROSCOELITE.

VANILLA is the dried fermented pod of certain orchids, indigenous to Mexico, but also found in Java, Réunion, the Seychelles, Brazil, Peru, on the banks of the Orinico, Parahyba and other rivers of South America.

The chief cultivated variety is *V. planifolia* (Andr.), which is grown on a considerable scale in Mexico, Réunion, Mauritius, the Seychelles, and in Java. The long fleshy stem of the plant clings by its aerial rootlets to trees, and bears a greenish-white flower. The fruit is a pulpy pod, about 6–12 ins. long and half an inch thick. In Mexico the plant is cultivated by planting cuttings at the feet of trees left in a clearing of the forest; these root in a few weeks and bear in the third year. In Réunion and in the Seychelles the plants are trained on trellis-work supported by trees, and are fertilised by hand. Care has to be taken to gather the pods at the proper time of maturity, as if over-ripe they split in drying, and if under-ripe they are deficient in flavour.

The fruit is usually gathered in the late autumn when full grown, but just before it ripens.

The curing of the fruits consists essentially of a slow process of drying in warm air, using either artificial or solar heat, but the details vary in different countries; thus in Mexico the gathered pods are allowed to lie in heaps until they begin to shrivel, after which they are heated, either by exposure to the sun or in ovens, when they gradually acquire a dark-brown colour. In Réunion the pods are immersed in boiling water for a few seconds, and then exposed to the sun for a few weeks in woollen cloths until they acquire the proper brown colour. As they become dry, they discharge a viscid liquid from the upper end, and are pressed from time to time to promote its flow. They are usually packed for the market in small bundles of fifty or one hundred in each.

It has also been suggested to use calcium chloride in the drying of the beans (J. Soc. Chem. Ind. 1898, 180).

For literature on the culture and curing of the vanilla beans, *v. ibid.* 1893, 707; *ibid.* 1896, 670; *ibid.* 1900, 847; *ibid.* 1901, 1048; *ibid.* 1906, 1117; *ibid.* 1909, 1002; Fr. Pat. 367285, 1906.

Those who habitually handle vanilla beans are often subjected to a cutaneous affection in the form of an eruption on the hands, face, or neck, which causes intense irritation; this is probably due to the oily juice which exudes from the beans. To avoid the affection, good ventilation of the factories and thorough washing of the hands are recommended (Claverie, J. Soc. Chem. Ind. 1908, 1082).

Commercial vanilla beans are almost black, 15–20 cm. long and 6–9 mm. thick. They are of a flattened cylindrical shape, tapering towards each end wrinkled and flexible. The best varieties, chiefly the Mexican, are the largest; they are very dark, glossy, and frost or *giore* (*i.e.* become covered with white crystals) very quickly. The inferior varieties are shorter, lighter in colour, and do not frost much.

Vanillons are the cured fruits of uncultivated vanilla plants; they are usually of poor quality. The unripe beans are said to contain coniferin and two enzymes, one of which converts coniferin into coniferyl alcohol and glucose, and the other oxidises the former to vanillin (Lecomte, Compt. rend. 1901, 133, 745).

Best Mexican vanilla beans contain 1·69–1·86 p.c. vanillin, Bourbon 1·91–2·90, Java 2·75, German East African 2·16, Ceylon 1·48, Tahiti 1·55–2·02, but the flavour of vanilla does not depend merely on the quantity of vanillin it contains (Busse, Zeitsch Nahr Genussm. 1899, 2, 519).

In addition to vanillin, the beans also contain vanillic acid $C_6H_3(OH)(OCH_3)CO_2H$, resins, fat, sugar, and 4–5 p.c. ash (Winton and Silverman, J. Soc. Chem. Ind. 1902, 1300; U.S. Pat. 931805; *ibid.* 1909, 1062; Gautier and Kling. Ann. Falsif. 1910, 3, 200). Anisyl alcohol and anisaldehyde have also been detected (Walbaum, Chem. Zentr. 1909, ii. 2181).

When the green vanilla pods are exposed to ultra violet rays, they emit a smell of vanillin, the process being accelerated by a rise in temperature and by previous immersion in dilute manganous chloride (Pougnet, Compt. rend. 1911, 152, 1184).

Tincture or essence of vanilla is formed by extracting the ground or cut up vanilla (10 parts) with a mixture of alcohol and water, and mixing the extract with 20 parts of refined sugar, the whole being made up to 100 parts.

The chief adulterant in vanilla extracts is coumarin, either artificial or from tonka beans: good imitation extracts may be obtained from 3 parts of vanilla, and 1 part of tonka beans, but most commercial imitations contain no vanilla, and are made up of artificial vanilla and coumarin and extract of tonka beans, the whole being coloured with caramel (Winton and Silverman, *l.c.*). In the preparation of inferior extracts weak alcohol and alkali are employed; these can be distinguished from good extracts by shaking a few c.c. with 3 volumes of water, when, if no alkali has been employed, a flocculent red precipitate will be formed. With hydrochloric acid a good extract should give only a slight turbidity (Hess, J. Amer. Chem. Soc. 1899, 21, 719).

Vanilla in the form of its tincture, is employed for flavouring chocolate and confectionery. It is also largely used in the manufacture of liqueurs and perfumes.

VANILLIN (Methoxyprotocatechuic aldehyde $C_6H_3(OH)(CHO)(OCH_3)[1:3:4]$) is contained in vanilla beans (*v.* VANILLA); in *Habenaria nigra* (R. Br.) (Lippmann, Ber. 1894, 27, 3409); in dahlia tubers (*ibid.* 1906, 39, 4147); in the woody parts of plants (*ibid.* 1904, 37, 4521); in the fruit and roots of *Avena sativa* [L.] (Rawton, Compt. rend. 1897, 125, 797). It also occurs in many other plants, in resins, balsams, and other substances (Campani and Grimaldi, Bull. Soc. chim. 1890, [iii.] 3, 458; Weld, Tollens and Lindsey, Ber. 1890, 23, 2990; Thomas, Arch. Pharm. 1899, 237, 271; Knitl, *ibid.* 256; Itallie, *ibid.* 1901, 239, 506). Vanillin may be obtained from vanilla pods by disintegrating the latter with sand and extracting with ether or a mixture of ether and alcohol (Tiemann and Haarmann, Ber. 1876, 9, 1287).

Vanillin may be obtained artificially by oxidising coniferin or coniferyl alcohol with chromic acid; by oxidising eugenol or, better, *iso*eugenol with air (Fr. Pat. 316526, 1902; Eng. Pat. 4909, 1902; J. Soc. Chem. Ind. 1902, 722; *ibid.* 1903, 439); with ozone or ozonised air (Trillat, Compt. rend. 1901, 133, 822; Bull. Soc. chim. 1903, 29, 45; Fr. Pats. 326775, 421784, 1909; U.S. Pat. 829300, 1906; J. Soc. Chem. Ind. 1903, 819); with peroxides (Eng. Pats. 11952, 1894; 14928, 1896; J. Soc. Chem. Ind. 1895, 506; *ibid.* 1897, 633); or electrolytically (Eng. Pats. 1624, 1895; *ibid.* 1896, 49, 292).

A 95 p.c. yield and a much purer product is said to be obtained by oxidising eugenol, *iso*eugenol, coniferin, or coniferyl alcohol, simultaneously with air and ultra violet rays at 50°–60° (D. R. P. 224071; J. Soc. Chem. Ind. 1910, 1036).

Vanillin may also be prepared by dissolving 14·2 kilos. protocatechuic aldehyde in concentrated sodium carbonate solution, and mixing it with 12·6 kilos. of dimethyl sulphate. The whole is heated on the water-bath, acidified, and extracted with ether. The latter is evaporated, and the vanillin extracted from the residue with chloroform (J. Soc. Chem. Ind. 1902, 274; *see* also *ibid.* 1897, 633; *ibid.* 1894, 1218; *ibid.* 1895, 1061).

Pure vanillin may be synthesised by the following method, the yield being 70–80 p.c. of the theoretical: 1 grm. molecule of a methyl or ethyl ester of mesoxalic acid or of any *aβ*-diketonic acid (or of the free acid), is added to a solution of 250 grms. of zinc chloride in 500 grms. of glacial acetic acid. The whole is kept at the ordinary temperature for 15 hours, after which it is heated at 50° for some hours, and then diluted with water and shaken with ether. The ethereal extract is washed with dilute aqueous sodium carbonate, distilled with steam to remove guaiacol (if present), and oxidised with copper chloride or acetate, vanilloylcarboxylic acid being formed. The latter, when heated with an equal weight of dimethyl-*p*-toluidine at 170°, yields vanillin, which is extracted from the acidified mixture by means of ether (Guyot and Gry, Compt. rend. 1909, 149, 928). Vanillin may also be synthesised by treating guaiacol with hydrocyanic acid, hydrochloric acid, and zinc chloride in the presence of infusorial earth (D. R. P. 189037; Chem. Zentr. 1908, i. 75).

Vanillin has also been prepared by other methods.

Literature.—Tiemann, Ber. 1891, 24, 2877; Augier and Boissien, Bull. Soc. chim. 1895, 13, 519; Bouveault, *ibid.* 1898, [iii.] 19, 75; Verley, *ibid.* 1901, [iii.] 25, 48; J. Soc. Chem. Ind. 1896, 556, 740; *ibid.* 1902, 68; *ibid.* 1908, 644; Stolz, Ber. 1904, 37, 4149; Frdl. 1877–87, i. 583–590; 1890–94, iii. 894–900; 1894–97, iv. 1273–1291; 1897–1900, v. 101, 110; 1902–04, vii. 755; 1905–07, viii. 1280, 1281; 1907–10, ix. 162, 1130, 1166.

Vanillin forms white needles having a strong characteristic taste and smell, m.p. 80°–81°, b.p. 285° (without decomposition in a stream of carbon dioxide) or 170°/15 mm. It is soluble in 90–100 parts of water at 14°, and in 20 parts at 75°–80°; it is readily soluble in ether, alcohol, and chloroform. The aqueous solution is acid, and gives a blue-violet colour with ferric chloride. When treated with ferrous sulphate and bromine water, vanillin is coloured bluish-green, then yellow (Pharm. J. 1897, 58, 167). Vanillin in hydrochloric acid gives characteristic colour reactions with phenols, ketones, and other substances; thus with acetone and its homologues a rose colour is formed, which becomes green on warming (Rosenthaler, Zeitsch. anal. Chem. 1905, 44, 292). A nitric acid solution of vanillin on standing yields a small quantity of hydrogen cyanide (Jorissen, J. Soc. Chem. Ind. 1910, 1036).

When oxidised with ferric chloride, nitric acid, or with fungus extract, or with gum arabic solution, vanillin forms *dehydrodivanillin*

$$[C_6H_2(CHO)(OCH_3)(OH)]_2,$$

white needles, m.p. 303°–304° (Tiemann, Ber. 1885, 18, 3493; *v.* Lerat, Bull. Soc. chim. 1904, [iii.] 31, 270; Bourquelot and Marchadier, *ibid.* 1248; Bentley, *ibid.* 1900, [iii.] 24, 942).

Vanillin may be estimated by converting it into its hydrazone by treatment with a hydrazide (Hanuš, Zeitsch. Nahr. Genussm. 1900, 3, 531, 657; *ibid.* 1905, 10, 585); or by converting it into its bisulphite derivative, decomposing the latter with sulphuric acid, removing the sulphur dioxide with a stream of carbon dioxide, then extracting the vanillin with ether; the ether is evaporated and the residue weighed (Busse, *ibid.* 1899, 2, 519). For other methods, *see* J. Soc. Chem. Ind. 1893, 718; *ibid.* 1903, 514.

Vanillin is frequently adulterated with coumarin, acetanilide, and with acetyl *iso*eugenol (Hess and Prescott, J. Amer. Chem. Soc. 1899, 21, 256; *see* also J. Soc. Chem. Ind. 1898, 1076; *ibid.* 1899, 604).

According to Winton and Lott (*ibid.* 1910, 1268) genuine vanillin may be distinguished from imitations by determining the lead number which, for the former, should lie between 0·29 and 0·34.

DERIVATIVES OF VANILLIN.

Vanillin forms salts with *zinc*, *lead*, *sodium*, and *magnesium* of the type $(C_8H_7O_3)M'$ (Tiemann and Haarmann, Ber. 1874, 7, 614).

Bromovanillin $C_6H_2Br(MeO)(CHO)(OH)$, m.p. 160°–161°, odourless, yellow leaflets (Tiemann and Haarmann, *l.c.*); the corresponding *iodo* compound has m.p. 174° (Bentley, Amer. Chem. J. 1900, 24, 172).

2-Nitrovanillin has m.p. 137°, **5-nitrovanillin** m.p. 176° (Bentley, *l.c.*; Pschorr and Sumuleanu Ber. 1899, 32, 3405).

Vanillin forms an *aldoxime*, m.p. 121°–122° (Decker and Klauser, *ibid.* 1904, 37, 520); a *phenylhydrazone*, m.p. 105° (Tiemann and Kees, *ibid.* 1885, 18, 1662); an *azine*, m.p. 174°–176° (Knöpfer, Monatsh. 1909, 30, 29); an *acetyl* derivative, m.p. 77° (Pschorr and Sumuleanu, *l.c.*); a *benzoyl* derivative, m.p. 75° (Wörner, Ber. 1896, 29, 143); also a *di*- and *trithio* derivative, in which the oxygen of the aldehyde group is replaced by sulphur, m.p. 129°–130°, 235°–237°, respectively (Manchot and Zahn, Annalen, 1905, 345, 320; Wörner, *l.c.*). *Vanillinacetic acid* $CHO{\cdot}C_6H_3(OMe)O{\cdot}CH_2{\cdot}CO_2H$ has m.p. 188° (Gassmann and Krafft, Ber. 1895, 28, 1871).

Vanillin-*p*-phenetidine (*eupyrin*)

$$OH{\cdot}C_6H_3(OCH_3)CH : N{\cdot}C_6H_4{\cdot}OC_2H_5$$

is formed by the interaction of vanillin and *p*-phenetidine at 140°; m.p. 97°. It is said to have hypnotic and antineuralgic properties (D. R. P. 91171, 96342; Frdl. 1894–97, iv. 1183, 1185).

Benzaldivanillin forms microscopic needles, m.p. 221·5°–222·5° (Rogoff, Ber. 1901, 34, 3881; *ibid.* 1902, 35, 1961).

Methyl ether of vanillin (veratraldehyde) $(CH_3O)_2C_6H_3{\cdot}CHO$ may be obtained by the methylation of vanillin, and by other methods. It is best to dissolve 1 mol. of vanillin in less than the equivalent quantity of 10 p.c. methysulphate on the water-bath, 1 mol. of potash in solution is then added in drops. When the reaction is over the solution is made slightly alkaline when it separates into two layers. The upper layer is extracted with ether, and on distilling off the latter, the pure aldehyde is obtained (Decker and Koch, Ber. 1907, 40, 4794). It has m.p. 47° (Juliusberg, *ibid.* 119), and possesses hypnotic properties. The corresponding *ethyl* derivative $CH_3O·C_6H_3(OC_2H_5)CHO$ has m.p. 64°–65° (Tiemann, Ber. 1875, 8, 1120). Homologues of vanillin have also been prepared (Eng. Pat. 10112, 1895; J. Soc. Chem. Ind. 1895, 595).

o-**Vanillin** (*m*-methoxysalicylic aldehyde) (CHO : OH : OMe=1 : 2 : 3) is, in the pure state, a solid which crystallises from water in pale yellow needles, m.p. 45·5°, b.p. 265°–266°. It dyes wool and silk from an acid bath a golden or lighter yellow, but the shades are not fast to soap (Noelting, Bull. Soc. Ind. Mulhouse, 1909, 79, 401; J. Pharm. chim. 1908, 28, 173).

It gives a phenyl hydrazone, m.p. 130°–131°, and a large number of other derivatives.

The root of a species of *Chlorocodon* of Uganda, where it is termed *Murando*, contains an odorous constituent $C_7H_5O_2·OMe$, m.p. 41°–42°, b.p. 257°–258°, which forms thin, colourless plate, is isomeric with vanillin, and yields an *oxime*, m.p. 138°, and a phenyl hydrazone, m.p. 137°–138° (Goulding and Pelly, Chem. Soc. Proc. 1908, 62).

VAPOUR DENSITY *v.* Specific gravity.

VAREC. *Kelp v.* Iodine.

VARIOLARIN *v.* Lichens.

VARISCITE. One of the many minerals consisting of hydrated aluminium phosphate, here with the formula $AlPO_4,2H_2O$. It forms concretionary and compact nodular masses, sometimes with a minutely crystallised (orthorhombic) surface. The colour is bright apple-green (due to chromium); sp.gr. 2·5–2·6; H. 4–5. It was first found in 1837 in Saxon Voigtland (the ancient Variscia), and within recent years has been mined in considerable quantities (3½ tons in 1909, and 2½ tons in 1910) at several places in Utah and Nevada. It is used as a gem-stone, taking the place of green turquoise (D. B. Sterrett, Min. Res. U.S., Annual Reports for 1910 and earlier). L. J. S.

VARNISH (*Syn. Vernis*, Fr.; *Lac. Firniss*, Ger.). A varnish may be described as a homogeneous fluid, which, when applied by any suitable means in a thin layer over the surface of any object, dries either by the evaporation of the volatile solvent, or by the combined evaporation of the volatile solvent, and the oxidation of the oil and resins to a more or less impervious elastic film unaffected by wear and tear, and by weather. Varnishes, in the drying of which heat is applied in a closed compartment so as to expel the solvent and then fuse the residual layer so that it is uniform like glass, are termed 'Japans.' A process has been patented for obtaining the necessary heat by generating it in the metal itself by the passage through it of an electric current. The simplest form of varnish is the spirit varnish, which is merely a solution of a more or less elastic solid in a volatile solvent. Spirit varnishes dry the most rapidly, but are liable to be brittle, and eventually to crack and peel off. Oil varnishes are, to a large extent, free from this defect, the drying oil which they contain binding and softening the resin, and although they take longer to dry, they are generally more lustrous and durable. When varnish is used as a vehicle or medium for the application of a pigment to an object, an enamel is produced. Such enamels dry with a gloss, and save labour by combining painting and varnishing in one operation. The solvents employed in making the various varnishes are chiefly methylated spirit, turpentine, naphtha, and petroleum spirit. Linseed oil is the oil in most general use, but tung oil (Chinese or Japanese wood oil) is now being employed, although its properties prevent its replacing linseed oil altogether. Walnut and poppy oils are also used, but only for certain special purposes. The solids, *i.e.* resins, &c., mostly employed in oil varnish making are: 1. Amber; 2. Copal, including Kauri and Manilla; 3. Rosin; 4. Asphaltum, including the various pitches. Pure resins are solid bodies, generally more or less coloured, amorphous or crystalline, which melt, as a rule, at a comparatively low temperature. They are insoluble in water, but partially or wholly soluble in a number of fluids such as alcohol, ether, chloroform, toluene, light petroleum, acetone, spirits of turpentine, &c.

Scale of hardness of varnish resins (Andés).

Oil Varnish Resins.

(A.) Amber.

(B.) Copal:—

Hard	Medium	Soft
1. Zanzibar	4. Sierra Leone fossil	17. Manilla
2. Mozambique	5. Angola red	18. Borneo
3 Madagascar	6. Benguela	19. Singapore
	7. Bastard Angola	20. S. American
	8. Copal pebble	21. Brazil
	9. Akra	22. Cochin China
	10 Benin	
	11. Loango	
	12. Gaboon	
	13. Congo	
	14. Sierra Leone ordinary	
	15. Angola white	
	16. Kauri	

Other (chiefly spirit) varnish resins.

1. Dammar
2. Shellac
3. Mastic
4. Sandarac
5. Rosin
6. Elemi
7. Oleo-resin turpentine
8. Burgundy pitch
9. Asphaltum.

The solubility of a resin may be said to be in inverse proportion to its hardness. The hard resins and semi-hard resins are but very slightly soluble in their original condition, working in the cold, but they are easily dissolved by spirits of turpentine, linseed oil, and other solvents by previously heating them in such a manner as to cause them to lose by destructive fractional distillation 10–25 p.c. or more of their weight of a resinous oil according to the resin dealt with. The partial destructive distillation of the harder resins is necessary before they dissolve in oil or other solvents. A great deal more oil must be distilled from hard resins before they become soluble than from soft resins.

The first process in preparing an oil varnish is the selection of the 'gum'; the pieces are sorted out by hand and graded according to their colour and general soundness, and as the gum gives the hardening properties to the varnish and is the most expensive constituent, great care is exercised in its selection. The selected gum is melted or 'run,' as it is called, and then caused to unite with the oil. To this end the gum is heated in a copper vessel over a rapid fire until it is perfectly liquid; a hood is placed over the pot and connected to large flues in which the varnish 'fumes' are condensed. The oil, specially chosen for varnish making, and clarified, is heated and cautiously added to the melted gum, the whole being kept well stirred, and the heating continued until the mixture is perfectly clear. If a drying oil has not been employed, the driers—lead and manganese compounds—are now carefully sprinkled in and the mixture further boiled with continual stirring until the drier has all dissolved. The pot is then removed from the fire, and when sufficiently cooled, turpentine is added gradually, stirring all the while until the whole is thoroughly mixed. A good deal of inflammable vapour is given off during these operations, and it is therefore necessary that the varnish house be so constructed as to carry away the vapours from contact with fire.

After thinning with turpentine, the varnish is strained into a tank, and allowed to stand until clear enough for use. The time required for this varies, and as all varnishes improve by age, the longer they are tanked the better. Old varnishes produce surfaces of much greater lustre than new ones, which are usually poor and dull. The good qualities of a varnish largely depend upon the efficient mixing of the gum and oil; if these are thoroughly incorporated, the varnish will be free from spots and blemishes on its surface, while if well boiled, a varnish is said to flow more freely and to dry more rapidly. Excessive boiling, however, causes the varnish to stouten and thus to require more turpentine to bring to working consistency, and the resulting fluid being poorer in its non-volatile constituents, yields a thinner and less lustrous coat. No strict rule on this point can be given, as some oils and gums stouten more rapidly than others, and the final result has to be manipulated according to circumstances.

The drying of oil varnishes varies considerably according to their composition, and the objects to which they have to be applied; thus a gold size may dry in a few minutes, while body or coach varnishes require 12–24 hours, and even then should be allowed 2 or 3 days to harden.

Of recent years many attempts have been made to prepare oil varnishes without previous fusion of the gum.

According to Coffignier, only one has led to successful results, viz. that in which naphthalene under pressure is employed. By this process, which was patented by Terisse, gums and resins such as copals are dissolved in naphthalene without melting the resin by heating under pressure to 250°–290°; linseed oil or other drying oil is added to the solution and the naphthalene distilled off. For example, 1 kilo. of Zanzibar resin is heated with 3 kilos. of naphthalene under a pressure of 4½ atmospheres at 290° for 2 hours; 250 grms. of linseed oil are added, and the mixture again heated under pressure at 290° for 45 mins., when it is filtered if necessary. 750 grms. of linseed oil heated to 220° are next added, and the mixture is distilled, exhaustion to a partial vacuum being resorted to as the temperature approaches 280°, at which point distillation will be finished. The varnish is completed by diluting the product with 2½ kilos. of thickened linseed oil and adding the requisite amounts of spirit of turpentine and drier.

Coffignier has compared the properties of a copal from Madagascar with those of the same rendered soluble by fusion and by heating with naphthalene under pressure. The advantages of this latter method—he states—are: (1) there is no loss of weight; (2) the resulting product is pale in colour; (3) its hardness is almost unimpaired. The effects of each process in the properties of the copal are shown in the following table—

	Original Copal	Fusion Process	Naphthalene Process
Sp.gr. at 16°C. .	1·058	1·062	1·061
Melting-point .	above 300°	205°	165°
Acid value . .	93·0	68·2	68·0
Saponification value	70·1	44·9	65·9
Percentage insoluble in—			
Ethyl alcohol .	73·8	91·8	74·4
Methyl „ .	79·6	93·3	86·8
Amyl „ .	22·4	66·7	12·8
Ether . .	65·0	51·8	19·7
Chloroform . .	69·0	1·7	soluble
Carbon tetrachloride . .	85·0	4·0	25·8
Spirit of turpentine	60·3	3·6	52·1
Acetone . .	64·3	84·8	65·0
Benzine . .	78·4	1·5	40·0
Aniline . .	17·8	gelatinous	soluble
Benzaldehyde .	21·8	2·0	„
Amyl acetate .	24·6	51·2	„

The manufacture of spirit varnishes is much less complicated than that of the oil preparations, the former being simply solutions of one or more resins in various solvents. On evaporation of the solvent a coating of varnish is obtained, consisting practically of the unchanged resins. The resins employed for this purpose are shellac, sandarac, soluble manilla, copal, dammar, benzoin, accroides, elemi, colophony, &c. The solution of the resins is effected either cold or hot as circumstances require, heat presenting the advantages of rapid solution and clearing, while the palest varnishes are obtained by the cold process.

To facilitate solution the gum should be kept continually agitated, thus preventing the particles of gum from forming a mass. It will be readily seen that the larger the surface of the gum exposed to the solvent the quicker will be the solution. For this purpose a revolving churn is used and the rotation keeps the particles in motion and prevents them from caking together. When the gum is all dissolved the varnishes are set aside to settle, and are ready for use almost immediately. They dry very rapidly, and are, generally speaking, harder and more brittle than oil varnishes, and as their drying is merely dependent on the evaporation of the solvent, the addition of 'driers' is not required.

Owing to the high price of shellac it is not surprising that inventors have directed their attentions to making artificial shellac, and a number of patents have been taken out, of which a few will now be mentioned.

1. *Fabr. de Prod. de Chim. organ de Laire*, 1905. Transparent synthetic resins which can be used in place of copal, amber, shellac, &c., are prepared by condensing commercial phenol or its homologues with formaldehyde or its homologues, and heating the condensation product in air, under pressure or *in vacuô*. For example, 10 parts of phenol are treated with 5–10 parts (7½ gave best results, L. M. N.) of a 40 p.c. solution of formaldehyde, and about 10 parts of 15 p.c. hydrochloric acid. The product is washed free from acid and excess of phenol, and the resulting plastic mass is heated for about half an hour at 140°.

2. *Birchoff*, 1906. An alcoholic extract of copal resin is mixed with olein, and the alcohol is distilled off from the product.

In an additional patent the use of other fatty acids, animal or vegetable oils, fats or waxes or mineral oils, soluble in alcohol, is put forward instead of olein.

3. *Englehardt and Beyersmann*, 1907. The process consists in heating resins at ordinary or increased pressure with a small quantity of aldehydes, simple or polymerised. For example, 6 kilos. of colophony, 3 kilos of gum sandarac, and 1 kilo of gum elemi, are melted, and 50 grms. of paraformaldehyde are added. The mass is heated until it becomes clear. The product is soluble in all the usual solvents.

4. *Farbenfabriken vorm. F. Bayer & Co.*, 1907. *o*-Cresol is heated for several hours at 100° with formaldehyde or substances capable of producing it, in the presence of acids and the cooled mass washed with water and purified by treatment with steam. The resulting product is a hard resin varying in colour from yellow to light brown, and melting at about 110°–128°. Used as a substitute for shellac, it gives varnishes which dry well on wood or metal. The hardness of the product depends upon the proportion of formaldehyde used.

5. *Meyer*, 1908. 400 parts of a resin or mixture of resins soluble in alcohol are treated with a solution of 60 parts of anhydrous sodium carbonate in 1000 parts of water, the mixture is boiled, then allowed to cool, filtered, and the filtrate added to a hot liquid prepared by dissolving 8 parts of stearin in 8 parts of a 33 p.c. solution of potassium hydroxide, and adding 80 parts of water. The mixture is neutralised with a mineral acid at a low temperature, the whole is stirred for some time, then heated to about 70°, filtered, and the precipitate washed and dried.

6. *Blumer*, 1908. The resinous products soluble in alkali, obtained by the condensation of phenols and formaldehyde, are treated in acid or alkaline solution with oxidising agents such as persulphates or perborates. The resulting products are odourless and differ from the original condensation products in that they are not affected by exposure to light and air. In their behaviour towards solvents the products resemble shellac.

7. *Loeschigk*, 1909. The 'foots' obtained in refining cotton-seed oil and similar products are oxidised in alkaline solution (*e.g.* by hydrogen peroxide) and then treated with acid, when the fatty matter separates from the remainder and may be recovered by means of a solvent: the residue is an amorphous resinous mass resembling shellac.

Natural varnishes or **lacquers.** Japanese lacquer (Urushi) is the milky juice that exudes from the trunk of the lacquer tree *Rhus vernicifera* (DC.). It seems that Chinese lacquer is obtained from the same tree, which is indigenous to, and growing wild in, central China at altitudes of 7000–7500 ft., and from which country it was transplanted to Japan in the remote ages. (*Cf.* LACQUER, vol. iii. 219.)

Burmese lacquer is obtained from a closely allied tree, *Melanorrhœa Usitata*.

On exposure to sunlight, or when warmed, the juice loses its moisture and becomes a brown, oily liquid to which oils, pigments, &c., are added to form the finished lacquer. Its chief constituent is urushiol. Miyama gives the following analysis for the Japanese lacquer: moisture 17·81–27·62, urushiol 64·14–77·63, gum 2·62–7·57, and nitrogenous matter 1·78–2·47. The lacquer collected during the summer is the best, and in the dried state contains 94·5 p.c. of urushiol. Chinese and Indian lacquer contain more moisture, more gum (23·5 and 37·78 p.c. in the Chinese and Japanese samples respectively), less urushiol (36·88 p.c. in inferior Chinese, and 26·39 p.c. in medium Indian). P. Sing, however, states that the principal constituent of Burmese lacquer, which he calls urushic acid, is identical with and equal in amount to the principal constituent of Japanese lacquer. The greater the proportion of urushiol, the better the quality of the lacquer, while the more gum there is the poorer the quality. The lacquer is obtained by tapping the trees, when a greyish-white juice exudes, which is collected in shells or other receptacles. These are covered with oil paper to protect the varnish from oxidation. Subsequently it is strained and exposed to the sun or heated slowly over a fire. The varnish then becomes brown and separates into two layers on standing. The upper or more fluid layer is used as a finishing coating over the ground layers. The nitrogenous matter contains an oxidising enzyme essential to the drying of the lacquer at low temperature. The drying process is retarded by raising the temperature above 50°, and it is suspended at 70°–80°, but at temperatures above 100° drying takes place without enzyme action in 4–5 hours, at 150° within 30 mins., and at 180° within 10 mins. In practice the best results are obtained by thinning the lacquer with turpentine oil or other solvent. As the layer turns brown at a high temperature, lacquers of light colour should be dried at 120°–150°, and even in the case of dark lacquers, the temperatures ought not to exceed 180°. The lacquered ware is prepared by applying several coats of an inferior quality of varnish mixed with pottery dust or dry powdered clay and rice paste. After each coat the ware is dried in a moist chamber and is then rubbed smooth with sandstone. The decorations are then applied in coloured lacquers. Since the lacquer blackens most pigments, only a limited number of coloured preparations is available. Of white pigments barium sulphate and bismuth oxychloride are used; red lacquers are prepared with vermilion and red oxide of iron; blue with prussian blue; yellow with cadmium sulphide, lead chromate and orpiment; green with chromium oxide; and black with lamp black or (to obtain a more brilliant layer) with iron powder or some compound of iron. A golden coating is obtained by lacquering the article with a mixture of 10 parts of finished lacquer, 1–3 parts of gamboge, and 5 parts of solvent and drying for about 2 hours in an oven at 120°.

Tung oil varnishes. Tung oil in combination with pigs' blood, constitutes what is known as Ningpo varnish, in colour a rich reddish-brown, and extensively used as a coating for woodwork in the Far East. It is stated to be very poisonous when moist to those who touch or even smell it. When dry, however, it is susceptible of a high polish, is very durable, and ornamental. *V.* TUNG OIL, p. 562.

In order to prepare tung oil for use in varnish making, it is necessary to heat it for some time at a high temperature, as the raw oil dries with an opaque film wanting in strength and elasticity. Great care must be exercised in heating the oil, as the whole charge may be wasted owing to sudden polymerisation which causes the mass to be changed into a more or less hard jelly which cannot be afterwards liquefied. The principal use for tung oil in varnish making is in combination with 'fused rosin' (calcium resinate), with which some very good varnishes for internal work can be produced.

According to a German patent (Sept. 8, 1908) tung oil may be converted into a product which gives a smooth, hard, lac-like coating. The oil is heated above its temperature of polymerisation, while keeping it in constant motion to prevent its solidifying. The product, which is of the same colour as the original oil, may be thickened in the same way as linseed oil, and when diluted with turpentine oil is said to yield varnishes possessing properties similar to those of the best copal varnishes.

Asphaltum. The chief asphaltums used for varnish making are manjak, gilsonite, Trinidad, Syrian, Egyptian, American, and West Indian. They are employed for preparing black japans, insulating varnishes, coach varnishes, &c.

In giving recipes for the preparation of varnishes, it is only intended to indicate the lines on which the varnish maker works, as each manufacturer has his own methods, which he guards jealously, and regards as secret processes.

Best body varnish for coachmakers. Fuse 8 lbs. of fine African gum copal, add 2 gals. of clarified oil previously heated, boil very slowly for 4 or 5 hours until quite stringy; thin with 3½ gals. turpentine, strain and tank. This gives a good elastic varnish; if required harder, substitute animé for part of the copal.

Best pale carriage varnish.

8 lbs. African copal
2½ gals. clarified oil
} boiled until stringy.

¼ lb. dried copperas
¼ lb. litharge
5½ gals. turpentine
} strained, &c.

8 lbs. animé
2½ gals. clarified oil
¼ lb. dried lead acetate
¼ lb. litharge
5½ gals. turpentine
} mix this to above while hot.

Pale oak varnish. Fuse 20 lbs. copal, and mix with 2 gals. hot drying oil, boil until it strings well, and thin with 5 gals. turpentine.

Leather varnish. Shellac 100 parts, sandarac 25, Venice turpentine 25, pale rosin 25, castor oil 20, nigrosin (spirit soluble) 15, spirit 790. The resins and colouring matters are placed in a shaking cask, and shaken with the spirit until dissolved, the varnish being then strained and bottled.

Varnish for tinfoil. 200 parts by weight of shellac are dissolved in about 700 parts of spirit, and filtered, the scum on the filter being allowed to drain, and a glass plate being used to cover the filter to prevent waste of the spirit by evaporation. This shellac varnish is incorporated, by stirring, with 100 parts of best white elemi resin and 25 parts of warm Venice turpenine. After filtration, the elemi resin left on the filter is pressed and returned to the filtrate. The resulting varnish can be stained, in the same way as the brilliant lacquers.

Coloured varnish for straw hats. A stock varnish is prepared from sandarac 35, elemi resin 54, pine resin 45, castor oil 11, and methylated spirit 850 parts. The crushed resins are suffused with the spirit in a suitable vessel, and left to dissolve, being shaken at intervals, the castor oil being added last of all. From this stock varnish, different coloured varnishes can be prepared by the addition of about 1 p.c. of aniline dye—aniline yellow, Bismarck brown, and ivory-black being the most suitable.

Inside oak varnish. Melt together 40 lbs. rosinate of lime, and 20 lbs. thickened oil, thin with 8 gals. turpentine, and add a little terebine.

Miller's india-rubber varnish. Caoutchouc 5 lbs., carbon disulphide 2½ lbs., spirit of turpentine 5 lbs. The rubber is cut into very small pieces and digested with the carbon disulphide in a glass retort in a sand-bath until complete solution is effected. Linseed oil is then heated, and while still hot, added to the above solution which, after cooling, is thinned down with the spirit of turpentine.

Dammar oil varnish. Dammar varnishes are soft, very flexible and transparent, but dry rather slowly. They are employed for inside work or upon metals, or on tissue paper, which they render transparent.

The proportion of the different ingredients varies as follows—

Dammar . . .	100 parts
Boiled linseed oil .	50–120 „
Spirit of turpentine .	200–500 „

The dammar is pulverised and dissolved hot in spirit of turpentine, and boiled linseed oil is run into the solution.

Wall paper varnish. 8 gals. linseed oil are heated to 340°F. until it ceases to froth; there are then added 32 lbs. rosin, 16 lbs. paraffin wax, 4 lbs. beeswax, and 1 pint copal varnish.

Asphaltum varnish for locks. Asphaltum 100 lbs., boiled linseed oil 5–16 lbs., spirit of turpentine 50–60 lbs. Melt the asphaltum and stir in the linseed oil and turpentine.

Asphaltum varnish for cycles. Fuse 50 lbs. Angola copal, add to it 41 lbs. boiled linseed oil. Pour the mixture into 200 lbs. of fused American asphaltum and boil until the mass draws out into threads. Then add 100 lbs. of a liquid drier and 336 lbs. spirit of turpentine.

Asphaltum varnish for wooden vessels. 200 parts asphaltum are dissolved in 900–1000 turpentine at moderate heat, and followed by 100 of elemi, 100 of yellow wax, and 100 of Venice turpentine; the whole being gently boiled for a ¼–½ an hour and strained when cold.

Varnish for rubber shoes. Hard rosin 5, shoemakers' pitch 15, Syrian asphaltum 15, coal tar 5, benzene 50, benzine 10 parts. The rosin, pitch, tar, and asphaltum are placed in a rolling cask, the benzene is poured over them, and the cask is rolled until all is dissolved, whereupon the varnish is thinned down with the benzine. Owing to the difficulty of straining the product, care should be exercised in selecting material free from impurities, otherwise the product will have to be left for some time to settle.

Varnishes for the production of drawing crayons—

(1) Sandarac 10 parts, alcohol (95 p.c.) 90 parts;

(2) Gum dammar 10 parts, alcohol 90 parts;

(3) White gum lac 5 parts, Venice turpentine 5 parts, alcohol 90 parts;

(4) Caoutchouc 2 parts, sandarac 8 parts, spirit of turpentine 45 parts, benzene 45 parts;

(5) Gutta-percha 2 parts, white gum lac 8 parts, benzene 40 parts, oil of turpentine 45 parts;

(6) Gutta-percha 3 parts, copal 7 parts, raw linseed oil 10 parts, spirit of turpentine 80 parts;

(7) Caoutchouc 1 part, dammar 35 parts, chloroform 6 parts, benzine 250 parts. A little sodium silicate is added to neutralise the acidity of the resin;

(8) An ammoniacal solution of casein, containing 10 p.c. of calcium tannate.

Best brunswick black. In an iron pot over a slow fire boil 45 lbs. asphaltum for at least 6 hours, and during the same time heat in another pot 6 gals. of oil which has been previously boiled. During the heating of the oil, introduce 6 lbs. of litharge gradually and boil it until it feels stringy between the fingers, then pour it into the pot containing the boiling asphaltum. Let the mixture boil until upon trial it will roll into hard pills, then let it cool, and mix it with 25 gals. turpentine or until it is of a proper consistency.

Photographic varnish. 1 part collodion is dissolved in 1 part of alcohol and 1½ parts of ether. The collodion must be perfectly dry before being dissolved.

Celluloid varnishes. Celluloid 5 parts, amyl acetate 16 parts, acetone 16 parts, ether 16 parts; celluloid 10 parts, amyl acetate 30 parts, acetone 30 parts, ether 30 parts, camphor 4 parts.

Dammar varnish. Dammar 20 parts, spirit turpentine 21–23 parts. This varnish is not quite transparent, but the addition of about 7½ p.c. by volume of absolute alcohol will remedy this defect.

Bookbinders' varnish. Shellac 10 parts, mastic or sandarac 9 parts, alcohol 50 parts.

Leather varnish. Shellac 10 parts, mastic, sandarac, or Venice turpentine 10 parts, alcohol 50 parts.

Floor varnish. Sandarac 50 lbs., orange shellac 80 lbs., methylated spirit 45 gals.

Paper varnish. Sandarac 50 lbs., Venice turpentine 30 lbs., methylated spirits 18 gals.

Rosin varnish for toys, &c. Rosin 20 parts, alcohol 95 p.c., 12·7–14·5 parts. To this may be added Venice turpentine 3–6 parts.

Varnish for stiffening felt hats. Water 200 parts, borax 15 parts, shellac 50 parts. The water is raised to boiling, the borax added, and then the shellac.

White label varnishes. White manilla copal 20 lbs., white rosin 10 lbs., methylated spirit 20 lbs.

Coffin varnish. Pale yellow rosin 18 lbs., manilla copal 12 lbs., methylated spirit 25 lbs. The varnish can be coloured brown or black with aniline dye.

Spirit copal varnish for leather. Methylated spirit 70 gals., Manilla copal 300 lbs., Venice turpentine 100 lbs., nigrosin 6 lbs. The nigrosin is dissolved in 3 gals. of spirit, the turpentine being dissolved in 8–10 gals. of the same solvent. The copal is dissolved in the remainder of the spirit, and the three solutions mixed.

Varnish for book leather. Grain lac 25 parts, sandarac 10 parts, white shellac 5 parts.

Dissolve in methylated spirit 82 parts. Add Venice turpentine 5 parts, filter and stir in 2 p.c. of castor oil.

Russian leather varnish. Sandarac 20 lbs., mastic 10 lbs., Venice turpentine 2 lbs., elemi 1 lb., castor oil 1 lb., birch tar oil 2 lbs., fuchsin or ponceau (for red) 1 lb., nigrosin (for black) 8 lbs., methylated spirit 20 gals.

For further information, *see* The Manufacture of Varnishes, vols. ii. and iii., by McIntosh, to which the writer is indebted for some of the above recipes.
L. M. N.

VARVICITE. *Hydrated manganese ore* $MnO_2 \cdot Mn_2O_3,H_2O$ (Rammelsberg), or

$$MnO \cdot 3Mn_2O_3,H_2O$$

(Phillips) (*v.* MANGANESE).

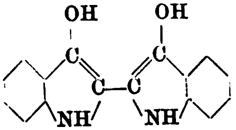
VASOTONIN. Trade name given to a combination of yohimbine and urethane which produces a fall of blood pressure, and appears to have considerable therapeutic value (Chem. Soc. Abstr. 1910, ii. 725).

VAT DYES. The term 'vat dye' is applied to those dyestuffs which, like indigo, are insoluble in water, dilute acids, and alkalis, but which, on being treated with suitable reducing agents, yield leuco compounds which are soluble in the hydroxides of the alkalis or of the alkaline earths, and in dyeing are taken up as such by textile fibres. By subsequent exposure to the air the leuco compound is oxidised on and in the fibre, with the re-formation of the original colouring matter. The characteristic fastness of the colours thus produced is, in a large measure, due to the insolubility of the dyestuff.

Indigo (*q.v.*), which was formerly the only known vat dye, is by far the most important of this series of colouring matters, and has been used in dyeing from time immemorial. A blue, dyed with it on cotton, is still referred to as a 'vatted blue,' whilst in the woollen industry, the term 'woaded blue' means a blue which is dyed either wholly or in part with indigo.

In preparing or 'setting' the indigo vat, various methods are employed in practice :

bring about the reduction of the indigotin. This is effected either by purely chemical or by bacteriological means, but in either case the product of the reaction is the same, viz. indigo white, $C_{16}H_{12}N_2O_2$, or graphically,



which dissolves in caustic soda with the formation of either the mono- or di-sodium salt ($C_{16}H_{11}N_2O_2Na$ or $C_{16}H_{10}N_2O_2Na_2$), according to the amount of caustic soda present in the bath. In aqueous solution, the mono-sodium salt has been shown to be an electrolyte, though it is not so strongly ionised as sodium chloride (Knecht and Batey, J. Soc. Dyers, 1910, 171).

The so-called chemical vats are distinguished, according to the reducing agent employed, as the copperas, the zinc, and the hydrosulphite vats. They are used in cotton dyeing, but the hydrosulphite vat also finds a limited application in wool dyeing. In the setting of any indigo vat, it is essential that the indigo should be in a finely divided state. The 20 p.c. artificial indigo paste contains the colouring matter in a sufficiently finely divided condition for the purpose, but the natural product must be ground, before use, to an impalpable powder.

The *copperas vat* depends upon the reducing action of ferrous hydroxide, and is made up of indigo, copperas and slaked lime. The lime reacting with the copperas forms ferrous hydroxide:

$$FeSO_4+Ca(OH)_2=Fe(OH)_2+CaSO_4$$

which in turn reduces the indigotin to indigo white:

$$2Fe(OH)_2+C_{16}H_{10}N_2O_2+2H_2O$$
$$=2Fe(OH)_3+C_{16}H_{12}N_2O_2$$

which then dissolves in the excess of lime present to form the soluble calcium salt. In the copperas vat, there is always a large amount of sediment, and to prevent this coming into contact with the goods during dyeing, deeper vessels are required than with the other chemical vats. At the present time, the copperas vat is not largely used in this country, the main reason being that its use involves a considerable loss in indigo.

In the *zinc vat*, zinc powder is the reducing agent. For satisfactory working, this should contain not less than 80 p.c. of metallic zinc. The vat is set with indigo, zinc powder and lime (or caustic soda). The reduction may be regarded as taking place as follows:

$$C_{16}H_{10}N_2O_2+Zn+2NaOH$$
$$=C_{16}H_{10}N_2O_2Na_2+Zn(OH)_2$$

although, according to Binz (Chem. Ind. 11, 1902), it is probable that combination of the indigotin with the alkali takes place first, with the formation of a compound $C_{16}H_{10}N_2O_2\cdot 2NaOH$, which then reacts with the zinc, forming the same products as shown in the above equation.

This vat is the one which is most largely used in cotton dyeing.

The *hydrosulphite vat* depends upon the reduction of the indigotin by sodium hydrosulphite, which is usually prepared by stirring zinc dust into commercial sodium bisulphite, in the proportion of a pound of the former to a gallon of the solution; and after allowing to stand for some time, adding to the solution an excess of milk of lime. The so-called 'stock vat' or concentrated vat is made by dissolving the indigo in this muddy liquid. (A product of this kind, containing about 3 p.c. of indigotin, was formerly sold under the name of 'reduced indigo.') This stock vat serves either for making up or for replenishing the dye vat proper. The reduction by means of sodium hydrosulphite may be regarded as taking place according to the following equation:

$$C_{16}H_{10}N_2O_2+Na_2S_2O_4+4NaOH$$
$$=C_{16}H_{10}N_2O_2Na_2+2Na_2SO_3+2H_2O$$

By employing artificial indigo paste, caustic soda, and the solid commercial sodium hydrosulphite, which is now placed on the market in an almost pure condition and at a reasonable price, it is possible to obtain a vat practically free from sediment.

The dyeing of cotton in the indigo vat is in itself a comparatively simple operation, although the management of the vat requires careful supervision and considerable practical experience. In hank dyeing, the wetted-out hanks are immersed in the vat and turned by hand under the surface of the liquid until thoroughly impregnated with the vat liquor, after which they are withdrawn and wrung, the liquor being returned to the vat. The hanks are then exposed freely to the air, in order to allow of the oxidation of the indigo white to indigotin. By repeating this operation several times, the shade becomes successively darker, and its depth will therefore depend upon the number of 'dips' in one and the same or in different vats. Although it is possible to obtain a dark shade by a single dip in a strong vat, this is not practised, because it would result in a large proportion of the indigo being loosely fixed and much of it would be lost in washing off; besides, the resulting blue would 'rub off' very badly. If lime has been used to render the vat alkaline, the goods are soured, after dyeing, in dilute sulphuric acid. In the dyeing of cotton warps and of piece goods, the material is guided through the vat by means of submerged rollers, so that it passes many times up and down between the time of entering and leaving; excess of liquor is expressed at the point of exit by means of a pair of squeezing rollers. In case it is desired to give the pieces two or more 'dips' in the same vat, they are stitched together, end to end, so as to form a continuous band, and, after leaving the vat, are passed up and down over a series of loosely running wooden rollers (which are usually placed immediately above the vat in order to economise space) for a sufficient length of time to allow of the oxidation of the indigo white before they re-enter the vat.

The reason why indigo white should be taken up from its aqueous solution by the cotton fibre is imperfectly understood. It has been suggested that it is a case of mutual precipitation between colloids, but as it has been definitely shown (see above) that indigo white lacks some of the most essential properties of a colloid, this theory cannot hold good. In any case, the affinity of indigo white for cotton is but slight as, when once taken up, it can be completely removed by continued washing with cold, air-free water, whereas a boiling solution of dilute caustic soda removes it from the fibre almost instantaneously. The affinity of indigo white for cotton appears to be similar in character to that of tannic acid for this fibre (Knecht and Nair, *ibid.* 1912, 28).

If the cotton to be dyed in indigo or other vat dyes has been previously mercerised, darker shades are obtained than on untreated cotton. The same applies with regard to indigo and certain indigoid dyestuffs if the cotton has been previously dyed manganese bronze or has been steeped for some time in strong nitric acid (see MERCERISING). In the latter case, the increase in depth is due in a greater measure to partial nitration of this fibre than to the mercerising effect of the acid.

Indigo dyed on cotton is sometimes associated with other colours. Thus, if a light shade of indigo is 'topped' or subsequently dyed chrome yellow, pleasing and very fast shades of green result. The old-fashioned 'fast black' was obtained by a combination of a heavy shade of indigo and catechu brown. The dyeing of a black of this description was practised by the Incas of Peru previous to the Spanish invasion.

Indigo dyed on cotton is usually regarded as fast to washing and to light. Strictly speaking, however, these qualities are only relative, for by repeated washing in soap or continued exposure to light, the colour (especially in light shades) gradually fades. But in fading it always retains the characteristic colour of indigo and does not change, as is the case with most other blues, to an unsightly grey or drab. It is noteworthy that the fastness of indigo to light may be considerably enhanced by treating the dyed fabric for a few minutes in a boiling dilute solution of copper sulphate.

In Egypt, Persia, India, China, Japan, and other Eastern countries, where dyeing is still almost entirely a household industry, fermentation vats are generally used for cotton dyeing. Such vats are occasionally used in this country for the dyeing of goods for certain markets. The fermentation vat imparts a certain peculiar smell to the goods dyed in it, and unless they possess this smell, the natives in some markets will not accept them as indigo-dyed.

The dyeing of *wool* with indigo differs from the dyeing of cotton in that whereas cotton is invariably dyed cold, the temperature of the vat for wool dyeing must be maintained at from 50° to 55°. Another point of difference is that in the case of wool, the time of immersion in the vat has to be much longer than in the case of cotton.

For wool dyeing, especially where fermentation vats are used, natural indigo is generally preferred to the artificial product.

Only one of the vats generally used in cotton dyeing can be used with advantage in wool dyeing, viz. the hydrosulphite vat. This is set with indigo, sodium hydrosulphite and ammonia. Although the cost of working this vat is greater, as far as materials are concerned, than that of the fermentation vats, this is more than compensated by its greater output. It is, however, only suitable for light to medium shades of blue.

The fermentation vats, of which a considerable variety are in use in different countries and sometimes in one and the same country, might appear at first sight to depend for their action upon different principles. But it is probable that in all cases the action depends upon a bacterial decomposition (butyric acid fermentation) of the carbohydrates, in which hydrogen is generated. Various substances containing carbohydrates, such as bran, flour, sugar, treacle or dates, are used along with lime, potash, or soda for the purpose. The setting and management of fermentation vats require considerable skill and experience, and in all large works these matters are under the sole control of the 'blue dyer,' upon whose intelligence and efficiency the prosperity of the works largely depends.

The fermentation vat mostly used in this country is the so-called *woad vat*, which is set in a vessel having a capacity of from 1600 to 3000 gals. with indigo, woad, bran, madder and lime, the temperature being maintained at 60°. The fermentation will have set in, as a rule, in from three to five days, and the vat will then be ready for use. Once set, a woad vat simply requires replenishing, from time to time, with the necessary additions of indigo, lime, and bran, and may remain in use continuously for many years. It should be explained that in this vat, the woad, which in former times (before the introduction of indigo from India) was the only indigo-bearing dyestuff used in this country and on the Continent, now acts solely by virtue of the bacteria which it contains, for in commercial woad there is, at the present day, no indigotin, the whole of the colouring matter having been destroyed by bacterial action.

Dyed on wool, indigo resists the action of light better than when dyed on cotton.

The disulphonic acid of indigotin, which is obtained by heating the dyestuff to about 100° with excess of concentrated sulphuric acid, is known commercially as indigo extract or, in the form of its sodium salt, as indigo carmine. It dyes wool 'at the boil' from a bath containing sulphuric acid and Glauber salt a much brighter shade of blue than that obtained in the vat, but the colour is neither fast to light nor to soap, and goods so dyed cannot be classed as being dyed with indigo.

Silk is seldom dyed in the indigo vat, although fast and pleasing shades can be obtained in this way.

Indigo in printing. In textile printing, notably in calico printing, indigo may be regarded as the most important individual dyestuff in use at the present time. This is partly due to the favour which it finds with the public as being pleasing to the eye and relatively fast, and partly to the variety of styles to which it lends itself in this branch of textile colouring. Effects are obtained with indigo in printing in three entirely different ways, viz. by direct printing, by the discharge process, and by the resist process.

In direct printing, the indigo is not printed on to the fabric in the reduced condition (a process which would obviously suggest itself at once to any one acquainted with its properties and its application in dyeing) owing to practical difficulties which this mode of application entails. The process in actual use is the so-called glucose process, in which glucose and caustic soda serve as the reducing agent. The pieces are first prepared by padding in a solution of glucose and are then dried. The finely ground indigo is made up with strong caustic soda thickened with maize starch and British gum. This is printed on to the prepared calico and the goods are run through a rapid ager containing air-free moist steam, the time required for this treatment being about half a minute. During the steaming, the indigo is reduced to indigo white which dissolves in the caustic soda and penetrates into the fibres. By subsequent exposure to air, the indigo white slowly oxidises back to indigo blue. The operations of preparing in glucose and drying may be dispensed with by adding to the printing colour a suitable reducing agent such as the formaldehyde compound of sodium sulphoxylate (hydrosulphite N.F.). This has no action on indigo in the cold, but reduces it on steaming for two to three minutes. The goods are then exposed to the air as in the glucose process.

In the discharge process, which lends itself to a greater variety of effects, the whole piece is first dyed to the required depth of blue in the vat and the colour is then removed locally either by destroying it by means of oxidising agents or by reducing it to the leuco compound and removing this by means of boiling dilute alkali. The former process, which is the one chiefly employed, consists in printing sodium chromate, suitably thickened, on to the blue fabric. After printing, the goods are run through a warm solution of sulphuric and oxalic acids, when in consequence of the liberation of chromic acid, the indigo is oxidised to isatin and this is removed in the subsequent washing, a white pattern on a blue ground resulting. For coloured discharges, the chromate is mixed with albumen and a suitable pigment, such as vermilion or chrome yellow, and the goods are run, after being printed, through the mixture of acids at a temperature high enough to coagulate the albumen. The fixation of the pigment and the destruction of the indigo thus take place simultaneously. The process is capable of many modifications. Thus, in order to obtain a bright scarlet on a blue ground, the indigo dyed fabric is padded first with an alkaline solution of β-naphthol, dried and printed with a colour containing diazotised *p*-nitraniline and sodium dichromate. The *p*-nitraniline red thus formed resists the action of the chromic acid formed when the pieces are run through acid and a bright red on a blue ground results.

Indigo may also be discharged by printing on sodium nitrate and running the goods through warm sulphuric acid of 100°Tw. (Freiberger's process).

In the reduction discharge process, the pieces are printed with the formaldehyde compound of sodium sulphoxylate with or without the addition of a catalyst such as anthraquinone. They are then steamed in the rapid ager to reduce the indigo and immediately run through a boiling bath of caustic soda, soda ash, or sodium silicate. The indigo white is thus completely removed and there is no tendering of the discharged places, as is invariably the case when the chromate discharge is used. In place of sulphoxylates, titanous thiocyanate may be used for this class of discharge.

In the resist process, the fabric is first printed with a mechanical or chemical 'resist,' and is then dyed in the vat. Wherever the resist has been printed no colour is fixed, and a white pattern on a blue ground results. In the East, and also to some extent in European print works, wax is used as the resist. After dyeing it is removed by soap and alkali. When the goods are handled (as in dyeing) after the wax has been printed on, the latter cracks in places so that in the dyeing some of the indigo liquor penetrates through the fissures, with the result that fine blue veins are afterwards seen in the pattern. This defect is characteristic of all true Battick work, which the modern printers are at pains to imitate. The resist mostly used at the present time is a very thick colour containing copper sulphate, lead nitrate, and China clay, usually thickened with flour and British gum and with or without the addition of such mechanical resists as tallow or rosin. As with the wax resist, the dyeing is best conducted in the zinc vat.

By increasing the amount of lead nitrate in this resist so as to exceed its equivalent in copper sulphate, and running the goods after dyeing through sodium dichromate, lead chromate is formed in the resisted parts and a yellow pattern on a blue ground results.

Vat Dyes other than Indigo.

Although it has long been known that indirubin (an isomeride of indigotin which occurs in almost all natural indigos) can be dyed in the same manner as indigo, it has never found any technical application, partly on account of the shade it yields being undesirable and partly for other reasons. Indophenol, which was discovered in 1882 by Koechlin and Witt, is also a vat dye, and although it was a commercial article in the 90's it was never much used, mainly because it produced loose colours, and it is now entirely obsolete.

The enormous development in the vat colour industry that has taken place during the last few years may be traced, on the one hand, to the discovery of indanthrene blue by Bohn in 1901, and on the other hand to the synthesis of thioindigo red by Friedländer in 1905. At the present time there are well over one hundred individual dyestuffs which may be strictly classed as vat dyes, without taking into account the large number of sulphide colours (*q.v.*) which, in a sense, might also be classed as vat dyes. It would obviously be out of place to embody the whole of our present knowledge of the vat dyes in this work, as that would require an amount of space which would not be commensurate with the general interest attaching to the subject. In the following, it will therefore be understood that the examples given are only typical of the various classes. For further information on the subject of vat dyes, see Engi, Chem. Zeit. 1908, 1178; Bohn, Ber. 1910, 987; Staeble, Chem. Zeit. 1910, 731 *et seq.*; Friedländer, *ibid.* 1911, 640; Masera, Färber-Zeit. 1911, 336; Grandmougin and Battegay, Els. Text. Bl. 1910, Malloch, J. Soc. Dyers, 1910, 26; Ermen, *ibid.* 1910, 56 and 236; E. de Barry Barnett, *ibid.* 1913, 183; Knecht, Rawson and Loewenthal, A Manual of Dyeing; Knecht and

Fothergill, The Principles and Practice of Textile Printing.

These vat dyes, other than indigo, may be classed under two headings, viz. as (*a*) indigoid dyestuffs, and (*b*) anthraquinonoid dyestuffs. The former come into the market under various trade names such as indigos of various brands, thioindigos (Kalle & Co.), helindone colours[1] (Meister Lucius & Brüning), ciba colours (Soc. of Chem. Ind., Basel), while the latter are generally classed as indanthrene colours (Badische Co.), algole colours (F. Bayer & Co.) or cibanon colours (Soc. of Chem. Ind., Basel). *V.* INDIGOID DYESTUFFS, Vol. III.

The bromo derivatives of indigotin are brought into the market under different designations, such as indigo pure R.B.N., ciba blue, indigo K2B, and generally yield, in dyeing and in printing, either redder or greener shades of blue than indigo itself, according to the amount of bromine which they contain. Thus, indigo 2R is 5 bromindigo, ciba blue 2B is 5 : 7 : 5′ : 7′-tetrabromindigo, and indigo KG consists mainly of 4 : 5 : 7 : 4′ : 5′ : 7′-hexabromindigo. The 6 : 6′-dibromindigo synthesised by Friedländer, and shown by him to be identical with the Tyrian purple of the ancients, is not a commercial article.

Of homologues of indigo, the 7 : 7′-dimethyl indigo (Indigo G) and naphthindigo (Ciba Green G) are so far the only commercial representatives.

Thioindigo red B or thionaphthene indigo

$$\mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{S}}>\mathrm{C}=\mathrm{C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{S}}>\mathrm{C_6H_4}$$

was discovered in 1905 by Friedländer and is obtained by fusing *o*-carboxyphenylthioglycollic acid with caustic potash. The discovery of this product marks the beginning of a new era in the history of organic colouring matters, for it opened up a new field and has already resulted in the introduction of a large number of new and valuable vat dyes. Like artificial indigo and most other commercial vat dyes, thioindigo red B comes into the market in the form of a 20 p.c. paste. The pure colouring matter is readily obtained from the dried paste by crystallisation from benzene or toluene and is obtained in well-defined dark red crystals. Its solution in benzene is red and shows a characteristic intense yellow fluorescence. In concentrated sulphuric acid it dissolves with a bluish-green colour; but on pouring the solution into water, the original dyestuff separates. By warming with fuming sulphuric acid, it is sulphonated and the soluble sulphonic acid thus obtained dyes wool from an acid bath a bluish shade of red. Unlike indigo, thioindigo red is not affected by oxidising agents, remaining unaffected by chromic acid, alkaline ferrocyanide and bleaching powder; whilst, on the other hand, it is more readily reduced than indigo. It has been shown that the reduction of thioindigo red to its leuco compound is analogous to that of indigo, two molecules of hydrogen or their equivalent being required for one molecular weight of the dyestuff (Knecht, J. Soc. Dyers, 1906, 156). Like indigo white, the leuco compound dissolves readily in caustic alkalis, forming a yellow vat from which it is taken up by the cotton fibre, the red reappearing on exposure to the air.

Of derivatives of thioindigo red, the following may be mentioned:

Thioindigo red B.G (dichlorthionaphthene indigo) $\mathrm{C_6H_3Cl}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{S}}>\mathrm{C}=\mathrm{C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{S}}>\mathrm{C_6H_3Cl}$; thioindigo red 3 B (dichlordimethylthionaphthene indigo)

$$\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{Cl}}>\mathrm{C_6H_2}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{S}}>\mathrm{C}=\mathrm{C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{S}}>\mathrm{C_6H_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{Cl}};$$

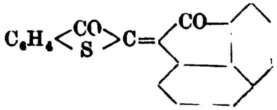
thioindigo violet 2B (dichlordimethyldimethoxythionaphthene indigo); *thioindigo orange R* (6 : 6′-diethoxythionaphthene indigo); and *thioindigo gray* (7 : 7′-diaminothioindigo)

Thioindigo scarlet R

$$\mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{S}}>\mathrm{C}=\mathrm{C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{NH}}>\mathrm{C_6H_4}$$

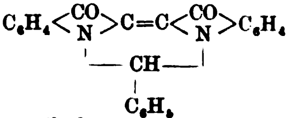
obtained by the action of hydroxythionaphthene on isatin may be regarded as a hemi-thioindigo. When acted upon by bromine in sulphuric acid solution it yields a dibromo derivative which is placed on the market under the name of thioindigo violet K. The tribromo-6-amino derivative represents thioindigo brown G.

Ciba scarlet G (also known as thioindigo scarlet 2G) is a non-nitrogenous product, obtained by the condensation of hydroxythionaphthene with acenaphthene quinone and has the constitution



By the bromination of this dyestuff, *Ciba red R* results.

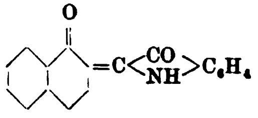
Of other indigoid dyestuffs, mention may be made of *Ciba yellow*, which is obtained by boiling indigo with benzoyl chloride and copper powder and to which the constitution



$$\mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{N}}>\mathrm{C}=\mathrm{C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{N}}>\mathrm{C_6H_4}\quad(\mathrm{N},\mathrm{N}{-}\mathrm{CH}{-}\mathrm{C_6H_5})$$

has been ascribed.

Alizarin indigo 3R, obtained by the condensation of *a*-naphthol with *a*-isatinchloride, is supposed to possess the following *ortho*-quinonoid structure



and is, in a sense, also indigoid in character. The corresponding derivative of *a*-hydroxyanthranol is known as *helindone blue 3GN*.

The indigoid dyestuffs all behave very much like indigo towards reducing agents, *i.e.* they yield leuco compounds (corresponding to indigo white) which dissolve readily in caustic alkalis, and in this condition show affinity for the textile fibres. The affinity of the different dyestuffs for the cotton fibre varies, however, in each case, so that their successful application

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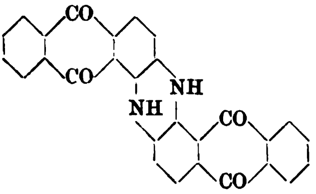
[1] Some helindone colours (especially browns and yellows) are anthraquinonoid in character.

especially in the production of mixed shades, requires a considerable amount of practical experience. The reducing agent employed for these colouring matters (in fact for all vat dyes other than indigo) is invariably sodium hydrosulphite, for although it is not the most economical, it is the most effective and convenient reagent for the purpose and yields vats which are free from sediment. In principle, the dyeing of cotton with these dyestuffs is the same as the dyeing of indigo in the hydrosulphite vat. The range of shades obtainable contains almost every colour of the spectrum, and some of these vie in brilliancy with the basic colours. Most of the colours are characterised by great fastness, and are in this respect superior to indigo. Hitherto no indigoid black has been produced.

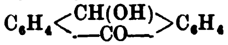
Although originally applied to dyeing and printing on cotton and other vegetable fibres, methods have been devised by which these colouring matters can be successfully applied in wool dyeing, by substituting ammonia for the caustic soda in the vat or neutralising the effect on the fibre of the caustic soda by the addition of some soluble oil (see H. Kämmerer, J. Soc. Dyers, 1913, 68).

In calico printing, the indigoid dyestuffs can be applied by methods similar to those employed for indigo, with the exception of the chromic acid discharge, which cannot be used owing to these dyestuffs being either not affected at all by chromic acid, on the one hand, or yielding imperfect discharges on the other. They can, however, be discharged by means of the formaldehyde compound of sodium hydrosulphite. For further information on the use of these colours in calico printing, see N. Evans, J. Soc. Dyers, 1913, 144.

Anthraquinonoid dyes. The first of these dyestuffs brought into the market was *indanthrene blue*, a product formed by the action of molten caustic potash on β-aminoanthraquinone, and possessing the constitution

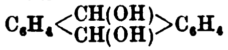


It is a dark blue compound insoluble in water, dilute acids, alkalis and most ordinary organic solvents. It can, however, be obtained in well-defined crystals from its solution in quinoline or by sublimation. Powerful oxidising agents convert it into the azine (containing 2 atoms of hydrogen less), but this is readily reconverted into the dyestuff by the action of reducing agents. Acted upon by hydrosulphite in presence of an excess of caustic soda, indanthrene blue yields a blue vat from which cotton and other vegetable fibres can be dyed in exceedingly fast shades of blue. The composition of the leuco compound of indanthrene blue is not known with certainty, but it is evident from the behaviour of anthraquinone, alizarin and the non-nitrogenous anthraquinonoid dyes that reduction takes place in the —CO— group, resulting in the formation of compounds analogous to hydroxyanthranol



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH(OH)}{CO}{>}C_6H_4$$

or dihydroxyanthranol

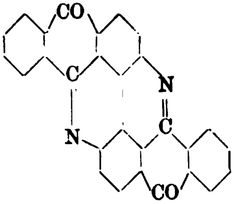


$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH(OH)}{CH(OH)}{>}C_6H_4$$

according to the extent of the reduction. To what extent the four —CO— groups of indanthrene blue suffer reduction in the formation of a 'vat' is not known at the present time, and this applies also to the other anthraquinonoid dyes.

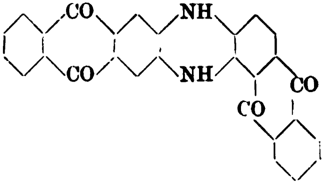
Halogen derivatives (Cl and Br) of indanthrene blue are also commercial articles and yield in dyeing greener shades of blue which are faster to bleaching powder than ordinary indanthrene blue (*v.* INDANTHRENE).

Flavanthrene or *indanthrene yellow* is formed as a by-product in the manufacture of indanthrene blue, but is obtained in much better yield, according to D. R. P. 138119, by the oxidation of β-aminoanthraquinone with antimony pentachloride in boiling nitrobenzene, or by the action of manganese peroxide in nitric acid solution (D. R. P. 141355). Flavanthrene has been shown to possess the constitution



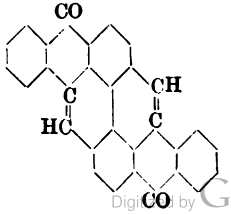
and comes into the market in the form of a yellow paste. With caustic soda and hydrosulphite (or other reducing agents) it yields a deep cobalt-blue vat from which cotton takes up the leuco compound and is dyed, after exposure to the air, a fast yellow. The halogen derivatives of flavanthrene dye redder shades than flavanthrene itself.

By the condensation of alizarin with 2:3-diaminoanthraquinone, a compound having the following constitution



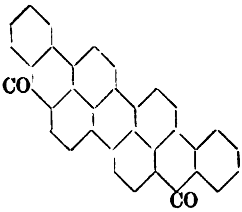
is obtained, halogen derivatives of which come into the market under the names *algol blue* and *algol green*.

That nitrog and ensulphur are not essential constituents of vat dyes is shown by the fact that *pyranthrone* or *indanthrene golden orange G*



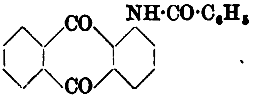
obtained by the condensation of two molecules of 2 : 2′-dimethyl-1:1′-dianthraquinonyl behaves in exactly the same manner towards reducing agents and in dyeing as the other vat dyes of this series. By the introduction of halogens into this dyestuff the shade is altered towards red. Thus, the brominated product represents *indanthrene scarlet G.*

By the alkaline condensation of two benzanthrone (or benzanthronequinoline) molecules, vat dyes are obtained, the simplest representative of which (*violanthrene* or *indanthrene violet*) is represented by the constitution

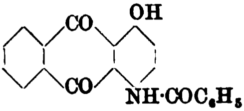


which, when nitrated, yields *indanthrene green* (D. R. PP. 172609, 185221).

Some of the dyestuffs of this series are derivatives of aminoanthraquinones and are represented by comparatively simple constitutional formulæ. Thus, *algol yellow N.G* is α-benzoylaminoanthraquinone



whilst *algol pink R* is the benzoyl derivative of a hydroxyaminoanthraquinone



It is noteworthy that the arylaminoanthraquinones do not act as vat dyes for cotton, although some of them are, in the form of their sulphonic acids, valuable wool dyes. In this connection it may be mentioned that whereas alizarin is quantitatively reduced by titanous chloride in presence of Rochelle salt to dehydroalizarin, alizarin orange cannot be reduced further than to β-aminoalizarin.

The anthraquinonoid dyes are employed in cotton dyeing much in the same way as the indigoid dyes. Generally speaking, they require, however, a much larger amount of caustic soda in the vat and are not dyed cold, but at a temperature of 50°–60°. In dyeing light shades, the dyebath is generally exhausted under these conditions. After dyeing, the goods are soaped hot, a process which in most cases considerably enhances the brilliancy of the colour. With some of the colours, the fastness to bleaching powder is increased by steaming under pressure after dyeing. Although no black anthraquinonoid dyestuff is known, a black of extraordinary fastness can be obtained on cotton by dyeing it first indanthrene green and then subjecting the dyed material to the action of bleaching powder. The colours obtained with the dyes of the anthraquinoid series are generally somewhat faster to light than those obtained with the indigoid dyes. They are not applicable to wool dyeing owing to the necessity of keeping the vat strongly alkaline with caustic soda with the inherent risk of damaging or destroying the fibre.

In calico printing, the anthraquinonoid dyes are largely used for some of the best classes of work. The usual method of using the indanthrene colours is to print a colour containing the vat dye, stannous chloride, ferrous sulphate and thickening, and after drying to pass rapidly through a hot strong solution of caustic soda. The fixation may also be effected in one operation by using a printing colour containing the vat dye, hydrosulphite-formaldehyde and soda ash, after which the goods are steamed for 5–7 mins. in air-free steam. The glucose process, as described for indigo, is also applicable to vat dyes in general.

By the introduction of the vat dyes the public demand for fast colours, especially in dyed and printed cotton and linen fabrics, has been met, and it is now possible to obtain by means of them almost any shade fast to washing, light, perspiration, rubbing, and even bleaching powder. It should, however, not be taken for granted that a vat dye is of necessity a fast colour. Those on the market have, however, generally been carefully tested and selected by the makers and usually possess this attribute. Many of the vat dyes are so fast that they can be put through the full bleaching process for cotton pieces without suffering any material diminution of intensity and brilliancy, and advantage is taken of this in the production of white fabrics with coloured stripes or figures. Whereas it was formerly necessary, in order to obtain these effects, to bleach both warp and weft before weaving, the bleaching is now effected in the piece and considerable economy is thus effected. With the exception of indigo, the vat dyes are still too expensive to admit of their being employed for any but the best class of work. This is due in part to the high cost of manufacture, but more especially to the fact that most of them are tinctorially weak, as compared with, for instance, the basic and direct cotton colours. Even indigo itself shows this drawback, but most of the other vat dyes show it to a much greater extent.

For the identification of the vat dyes in dyed and printed fabrics, see A. G. Green and G. H. Frank (J. Soc. Dyers, 1910, 83), also G. E. Holden (*ibid.* 1909, 47). Indigo can readily be distinguished from the other vat blues by dissolving the fabric in warm 80 p.c. sulphuric acid. The solution is poured into water and filtered through a small asbestos filter. After washing and drying, the residue on the filter is heated to about 100° with concentrated sulphuric acid and again poured into water and filtered. Under these conditions, the indigo is sulphonated and passes into the filtrate with a bright blue colour, whereas the other vat blues remain unaffected.

E. K.

VAUQUELINITE. Native lead and copper chromate.

VEGETABLE BUTTER *v.* BASSIA OILS; also OILS, FIXED, AND FATS.

VEGETABLE ETHIOPS. A form of charcoal obtained by the incineration of *Fuci.*

VEGETABLE FATS *v.* Oils, fixed, and fats.

VEGETABLE IVORY. The fruit of *Phytelephas macrocarpa* (Ruiz. and Pav.) found in Columbia, South America.

VEGETABLE PARCHMENT *v. Parchment paper*, art. Cellulose.

VEGETABLE SPERMACETI. *Insect wax, v.* Waxes.

VEGETO-ALKALOIDS. The vegetable alkaloids are nitrogenous carbon compounds possessing basic properties. They occur in plants, usually as the salts of organic acids. The greater number of them contain carbon, hydrogen, nitrogen, and oxygen, but in a few cases oxygen is absent, *e.g.* nicotine, coniine. Chemically the vegetable alkaloids belong almost entirely to six groups: (1) derivatives of piperidine, *e.g.* nicotine, coniine; (2) derivatives of a condensed pyrrolidine—piperidine nucleus, *e.g.* hyoscyamine, cocaine; (3) derivatives of quinoline, *e.g.* quinine, strychnine; (4) derivatives of *iso*quinoline, *e.g.* papaverine, corydaline, morphine, thebaine; (5) derivatives of cyclic nuclei containing 2 nitrogen atoms, *e.g.* caffeine, theobromine, pilocarpine; (6) derivatives of aliphatic amines, *e.g.* choline.

The discovery of these bodies is due to the German pharmacist, Sertürner, who, about the year 1807, isolated from opium a basic, salt-forming substance, to which he gave the name 'morphium.' The principal physiological action of opium was found to be exerted by this substance, which is now called morphine. The isolation, from other medicinal plants, of similar compounds capable of producing the physiological effect of the plants themselves quickly followed the discovery of morphine, and in the next few years strychnine and brucine were isolated from *Strychnos Nux-vomica* seeds, and quinine and cinchonine from cinchona bark by Pelletier and Caventou. The first volatile alkaloid, coniine, was obtained from hemlock in 1827 by Giesecke, and in the following year nicotine was described by Posselt and Riemann. At the present day a very large number of vegetable alkaloids are known, and the list is being extended every year.

Distribution and mode of formation. Plants yielding alkaloids are widely distributed throughout the vegetable kingdom, but it is remarkable that of the two great sub-divisions of flowering plants, viz. monocotyledons and dicotyledons, the former yield very few alkaloids, the great majority being derived from dicotyledonous plants. In the latter sub-division certain orders are poor in alkaloids, *e.g. Labiatæ*, and *Graminaceæ*, whilst the *Ranunculaceæ*, *Solanaceæ*, and *Papaveraceæ* are typically rich in alkaloids. The gymnosperms, ferns, and fungi furnish few alkaloids, and the algæ and the mosses are devoid of such constituents.

Two chief views have been held as to the function of alkaloids in plants: (1) that they are ultimate products of metabolism, and (2) that they are plastic materials capable of further utilisation by plants in which they occur; but the whole of the recorded facts cannot be accounted for by either theory.

The proportion of alkaloid generally reaches its maximum when the plant is mature.

Alkaloids are distributed throughout the various members of a plant, being found in the leaves, flowers, and seeds, as well as in the root and bark, but the amounts found in the different parts may show great variation. When a plant dies down after flowering, the alkaloid often accumulates in the root, whilst during the growth of a tree the alkaloids appear to be gradually deposited in the bark, and have, therefore, been compared to the excreta of animals.

Very little is known as to the actual mode in which alkaloids are formed in plants. It has been suggested that they may originate in (1) decomposition of proteins, (2) in the condensation of pyrones with ammonia to form pyridine derivatives, (3) in the condensation of ketones and aldehydes with ammonia. The experimental investigation of the natural mode of formation of alkaloids is beset with the great difficulty that the intermediate compounds, the precursors of alkaloids, are present only in minute quantity, and are hard to separate unchanged from the various plant constituents with which they are associated (*cf.* Czapek, Biochemie der Pflanzen, 1905, ii. 267; Pictet, Arch. Sci. phys. nat. 1905, 243, 329; 1906, 244, 389; Tunmann, Arch. Pharm. 1910, 248, 644; Winterstein und Trier, Die Alkaloide, 1910, 263).

Plants often contain several alkaloids, which, however, are generally found to be more or less closely related in chemical structure.

Method of extraction. Various processes are employed for the extraction of alkaloids from plants, the nature of the process depending partly on the properties of the alkaloid which has to be extracted, and partly on the nature of the other substances which occur with it. In the older processes the finely powdered part of the plant (root, bark, &c.) was exhausted by percolating it with dilute sulphuric or hydrochloric acid, which decomposed the natural organic salt of the alkaloid, forming a sulphate or hydrochloride readily soluble in water. The alkaloid was precipitated by the addition of an alkali to this solution; or the plant was incorporated with lime or magnesia to liberate the alkaloid, and the dry mass exhausted with a suitable solvent, generally alcohol. Now that it is known how readily some alkaloids are hydrolysed and otherwise altered by strong acids, the use of mineral acids has been abandoned except in a few cases, and where extraction with an acid medium must be resorted to, dilute solutions of acetic or tartaric acid are employed. In general the natural alkaloidal salts are now extracted directly with alcohol or other organic solvent, and after the solvent has been distilled off, water or very dilute sulphuric acid is added, and from this solution the alkaloid is liberated by the addition of a weak alkali, and extracted by means of an indifferent solvent, such as chloroform or ether, from which it may be recovered by distilling off the solvent. From such residues the pure alkaloid is obtained by fractional crystallisation of suitable derivatives. In the cases of certain very stable alkaloids admixture of the plant with lime or magnesia and extraction of the dry mixture with an organic solvent can be safely employed, and in other cases (*e.g.* caffeine in tea) extraction with boiling water may be resorted to. Ammonia or an alkali bicarbonate is to be recommended for precipitating alkaloids in place of potash or soda. The use of animal charcoal for decolorising alkaloidal solutions requires caution, since some alkaloids adhere to this substance, more especially when they are in the free state.

When the alkaloid is volatile the parts of the plant are mixed with very dilute alkali and steam distilled; the liberated alkaloid condenses with the steam, and may be extracted with a suitable solvent from the aqueous distillate.

Further information respecting the extraction of alkaloids from plants will be given in connection with the account of each alkaloid. The worker should also consult the original memoirs there referred to.

Purification and separation of alkaloids. An alkaloid having been isolated in a pure state (*i.e.* free from non-alkaloidal substances), it is necessary to obtain evidence of its being a single substance before its composition and properties are investigated. This may be done by crystallising the alkaloid or one of its salts in several fractions, the properties of each fraction being examined; they should, of course, be identical if the alkaloid is homogeneous. The melting-point is conveniently made use of for this purpose, or, when this is not sharply defined, some other physical property, *e.g.* rotatory power, solubility, &c. The so-called colour reactions are of very little value for this purpose.

In cases where a distinctive physical property cannot be found, combustions must be made of the different fractions in order to determine whether their composition is identical. The aurichlorides have frequently proved useful as a means of characterising and purifying alkaloids, since these compounds, as a rule, are easily prepared, crystallise well, and melt sharply, each at a different temperature, even when the alkaloids themselves are closely related. An aurichloride having been obtained of constant melting-point, *i.e.* not changed by recrystallisation, the corresponding alkaloid may be regenerated from it by precipitating the gold from it, suspended or dissolved in water, with the slightest possible excess of hydrogen sulphide, filtering, expelling any trace of hydrogen sulphide, and then recovering the alkaloid from the solution of the hydrochloride in the usual manner. For further information concerning the methods of separating and characterising alkaloids, *see* Dunstan and Read on the alkaloids of Japanese aconite (Chem. Soc. Trans. 1900, 77. 45); Dunstan and Brown on hyoscyamine in *Hyoscyamus muticus* (Linn.) (*ibid.* 1899, 75, 72); Watt on the alkaloids of *Senecio latifolius* (Banks and Soland) (*ibid.* 1909, 95, 466); Jowett on the alkaloid of *Aconitum heterophyllum* (Wall.) (*ibid.* 1896, 69, 1518).

Physical and chemical characters and constitution of the vegetable alkaloids. The vegetable alkaloids are, in general, solid substances, most of them being crystalline. A small number are liquid (coniine, nicotine, pilocarpine, &c.); some of these, being volatile, distil with water, although alone they boil at much higher temperatures, often without appreciable decomposition. The crystalline alkaloids generally melt with decomposition, but sufficiently sharply to permit of the melting-point being used for their identification.

Most of the vegetable alkaloids are optically active. The greater number are lævorotatory. A few are dextrorotatory, notably aconitine, pilocarpine, and cinchonine. A few of the alkaloids are optically inactive, *e.g.* piperine, berberine, and papaverine. The alkaloidal salts generally exhibit the same kind of optical activity as the alkaloids themselves; but the salts of the lævorotatory nicotine and narcotine are dextrorotatory, whilst the dextrorotatory aconitine furnishes lævorotatory salts.

The majority of the vegetable alkaloids are insoluble, or very sparingly soluble in water; their best solvent is alcohol. Usually they are also dissolved by chloroform, less generally by ether, benzene, or amyl alcohol, sometimes by light petroleum. Their aqueous solutions are frequently strongly alkaline to litmus, and precipitate hydroxides from solutions of metallic salts. Certain of the alkaloids, *e.g.* morphine, are soluble in alkali hydroxides.

Like ammonia, the vegetable alkaloids combine directly with acids to form salts, which are usually crystalline, and often soluble in water or alcohol, but generally insoluble in chloroform or ether.

In their combinations with acids the alkaloids nearly always act as monacidic bases, even when they contain two atoms of nitrogen in the molecule, that is to say, they unite in only one proportion with acids to form stable salts. To this rule, however, notable exceptions exist, especially among the cinchona alkaloids; *e.g.* quinine is a diacidic base.[1]

The ordinary salts will be alluded to later in connection with the particular alkaloids. Attention will be directed here to certain alkaloidal compounds, which are important in connection with the detection and identification of the vegetable alkaloids.

Auric chloride $AuCl_3$ combines with the hydrochlorides of the alkaloids, forming well-defined aurichlorides,[2] usually composed of one molecule of the alkaloidal hydrochloride and one molecule of auric chloride, $B\cdot HCl\cdot AuCl_3$. These compounds are frequently sparingly soluble in water, and are thrown down as pale-yellow

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[1] The nomenclature of alkaloidal salts is in a very unsatisfactory state. They were originally named after the similar compounds of ammonia, viz. hydrochlorate, sulphate, nitrate, etc. These names have long ceased to be used for the ammonia compounds, which are now regarded as salts of 'ammonium,' viz. ammonium chloride, ammonium sulphate, etc. No analogous change has, however, been made in the names of alkaloidal salts, the salts of morphine, for example, being still called morphine hydrochlorate (or hydrochloride), morphine sulphate, etc., and not morphium chloride, morphium sulphate, etc. The only change that has been made is to alter 'hydrochlorate,' not into 'chloride' but into 'hydrochloride,' which has the advantage of indicating that the compound contains the extra molecule of hydrochloric acid, and in this respect differs from the metallic chlorides. This reform has been extended to the 'hydriodates' and 'hydrobromates,' which are now called 'hydriodides' and 'hydrobromides.' It has not, however, been applied to the other salts (sulphate, nitrate, etc.), which, though similarly constituted, are not termed 'hydrosulphates,' 'hydronitrates,' etc.

[2] Compounds of the alkaloidal hydrochlorides with auric chloride will be called *auri-chlorides*, the corresponding compounds with platinic chloride, *platinichlorides*, and with mercuric chloride, *mercuri-chlorides*. A compound of the alkaloid itself with auric chloride will be termed an *auric chloride compound*, or simply (for example) pilocarpine auric chloride, and the similar *mercuric chloride compound*, pilocarpine mercuric chloride.

precipitates, when an aqueous solution of auric chloride is mixed with an aqueous solution of the alkaloidal hydrochloride. Sometimes the aurichlorides are soluble in water. They may be crystallised from their solution in alcohol or water acidulated with hydrochloric acid. As has been pointed out already, these crystalline compounds melt sharply, and are often useful in characterising alkaloids. They are also conveniently employed in ascertaining the formula-weights of the alkaloids, the gold being determined by ignition. In cases where neither the alkaloid nor one of its ordinary salts can be crystallised or readily obtained pure, the percentage composition of the alkaloid may be arrived at from the results of the combustion of the pure aurichloride. When only small quantities of material are available, it is possible to determine the composition of the aurichloride without losing the alkaloid, by the following process. A weighed quantity of the aurichloride (0·5–1 grm.) is dissolved or finely suspended in water, and decomposed by the gradual addition of a very slight excess of aqueous hydrogen sulphide. The resulting precipitate of gold sulphide is washed, dried, ignited, and the residue of gold weighed. The filtrate and washings are made alkaline with ammonia, and the alkaloid extracted by agitation with chloroform or ether; the residue of alkaloid left on the evaporation of the solvent is dried and weighed. The alkaline, aqueous solution is now strongly acidified with nitric acid, and the chlorine precipitated with silver nitrate in the ordinary manner and weighed as silver chloride.

Auric chloride combines with the alkaloids themselves, as well as with their hydrochlorides, forming auric chloride compounds $B{\cdot}AuCl_3$, which are stable crystalline salts composed of one molecule of the alkaloid and one of auric chloride. They are obtained by mixing together alcoholic solutions of the alkaloids and auric chloride. The determination of the melting-point and composition of these compounds furnishes an additional means of characterising certain alkaloids. So far these compounds have only been prepared from a few alkaloids (Dunstan and Ince, Chem. Soc. Trans. 1891, 59, 271; Hardy and Calmels, Bull. Soc. chim, 1887, [ii.] 18, 220), but there is reason to believe that they are obtainable from many of the vegetable alkaloids.

Aurichloro derivatives of caffeine and certain of the benzaoconines have been obtained. They are produced from the aurichlorides by the loss of 2 mol. props. of hydrogen chloride, and may therefore be regarded as derived from the alkaloid by the replacement of one atom of hydrogen by the group $AuCl_2$ (Dunstan and Shepheard, Chem. Soc. Trans. 1893, 63. 201; Dunstan and Harrison, *ibid.* 1893, 63, 443; Dunstan and Read, *ibid.* 1900, 77, 57).

Bismuth iodide or *cadmium iodide* dissolved n aqueous potassium iodide precipitates alkaoids, and may be used as a general alkaloidal eagent like iodine solution or Mayer's reagent *see* below).

Iodine, dissolved in aqueous potassium iodide precipitates the solutions of most alkaloidal alts, and may be used as a general reagent for he detection of alkaloids. The precipitate is eddish-brown when the solution is dilute, but in strong solutions this precipitate at once aggregates to a greenish-black mass. The precipitates consist of the periodides of the alkaloids ($B{\cdot}HI{\cdot}I_2$ or ${\cdot}I_4$). Many of them crystallise well from alcoholic solution, the crystals being green by reflected, and red by transmitted, light. The alkaloids may be recovered from these periodides most safely by dissolving the latter in aqueous sodium thiosulphate, then adding excess of ammonia, and shaking out the alkaloid with ether or chloroform (Dunstan and Ransom, Pharm. J. 1883–4, [iii.] 14, 623).

Mercuric chloride also forms double salts with certain alkaloids.

Mercuric iodide dissolved in aqueous potassium iodide (Mayer's reagent) produces an abundant yellowish-white, flocculent precipitate of indefinite composition, in solutions of nearly all alkaloidal salts, and for this reason is one of the best general reagents for detecting alkaloids (Mayer, Chem. News, 1863, 7, 159). The precipitation of an alkaloid by this reagent is often quite complete if certain precautions are taken, the character of which varies with different alkaloids, some being completely precipitated only when the alkaloidal solution is neutral, others requiring that the solution shall be faintly acid to complete the precipitation, while a few alkaloids are only precipitated by this reagent from a strongly acid solution. Although the precipitates (double iodides of mercury and alkaloids) produced by this reagent have not a constant composition, yet the quantity of a known alkaloid contained in a given solution may be volumetrically estimated by its means, the precipitatory power of a cubic centimetre of the solution under prescribed conditions having been previously found for the alkaloid in question. The alkaloids may be recovered from these precipitates by suspending them in water, and passing hydrogen sulphide through the mixture. After filtering off the mercuric sulphide, a solution of the alkaloidal hydriodide is obtained, from which the alkaloid may be liberated and extracted in the usual way.

Phosphomolybdic acid, prepared by adding excess of nitric acid to a solution of sodium phosphomolybdate, produces a white precipitate with solutions of most alkaloidal salts (Sonnenschein, Annalen, 1857, 104, 45). *Phosphotungstic acid* acts similarly. Alkalis liberate the alkaloids from these precipitates.

Picric acid precipitates the solutions of most alkaloidal salts, and the yellow picrates may often be crystallised; in very acid or dilute solutions the precipitation of the picrate is frequently not observed. The alkaloids may be recovered from the picrates by decomposing them with aqueous alkali, and extracting the liquid with ether or chloroform.

Picrolonic acid (4-nitro-1-*p*-nitrophenyl-3-methyl-5-pyrazolone) in alcoholic solution furnishes with many alkaloids crystalline derivatives of definite melting-point (Warren and Weiss, J. Biol. Chem. 1907, 3, 327), and may be used as a means of identification in such cases.

Platinic chloride combines with alkaloidal hydrochlorides to form platinichlorides

$$(B{\cdot}HCl)_2PtCl_4,$$

which are sometimes precipitated when aqueous solutions of those substances are mixed, but are generally more soluble than the corresponding aurichlorides. They frequently crystallise well, and are useful in determining the formula-weights of the alkaloids, the platinum being estimated by carefully igniting the salt and weighing the metallic residue.

Tannic acid also precipitates solutions of many alkaloidal salts.

For a full discussion of these and other alkaloidal reagents, *see* Allen's Commercial Organic Analysis, 4th ed., vol. vi.

Detection of alkaloids. The presence of an alkaloid may be detected by the use of the general reagents referred to above, which, as a rule, afford most delicate indications when added to a slightly acidified solution. The evidence thus obtained must be supplemented by isolation of the alkaloid and an examination of its chief chemical properties. Many of the alkaloids give characteristic colour reactions when mixed with sulphuric acid and other reagents; these will be alluded to later in connection with each alkaloid. It should, however, be remembered that, with possibly one or two exceptions, colour reactions cannot be relied on as conclusive proof of the presence of a particular alkaloid, since very similar colour reactions are often given by more than one alkaloid, and, on the other hand, distinctive colours are frequently obscured by the presence of impurity.

For the detection and separation of alkaloids in toxicology special processes are used, which in principle are the same as those employed to extract alkaloids from plants, but are longer, and differ somewhat in the mode of procedure. The methods devised by Stas-Otto, by Dragendorff, and by Erdmann and Uslar are those usually resorted to. For details of these methods the following works should be consulted: Husemann, Toxicologie; Dragendorff, Gerichtlich-Chemische Ermittelung von Giften; Taylor's Toxicology, edited by Stevenson; Wynter Blyth, Poisons, their Effects and Detection, 1909; Kippenberger (Zeitsch. anal. Chem. 1895, 34, 294).

It will not be possible within the limits of this article to give an account of every known vegetable alkaloid, but only to allude to most of those which are of practical importance in some connection or another, because they are manufactured on a large scale, or are used largely in medicine, or on account of the familiarity of the plants which yield them, &c. Even in these cases it will be impossible to do much more than afford an outline of the principal properties, reactions, modes of preparation, detection, and estimation of the most important alkaloids. Processes for the extraction, detection, and estimation of important alkaloids, as a rule, will be somewhat fully described, whilst questions relating to their chemical constitution, although not exhaustively discussed, will, in important instances, be dealt with sufficiently to make clear the character of the evidence that has been utilised in effecting the remarkable progress of the last 20 years. References will be given to the original memoirs from which fuller information may be obtained.

Since it is not possible to adopt a chemical classification of more than a few of the vegetable alkaloids, and as a system of classification founded on that of the plants which yield them would be without significance in a chemical dictionary, the principal alkaloid will be considered in alphabetical order, excep in cases where several alkaloids are furnishe by one plant, when these will, as a rule, be con sidered in connection with the principal alkaloid

ACONITINE AND THE ACONITE ALKALOIDS.

The alkaloids of the various species o *Aconitum* which have been examined chemicall fall into two sharply differentiated groups. Th first, of which aconitine itself is the type, include a number of highly toxic alkaloids (*the aconi tines*), which are diacyl esters of a series o polyhydroxy bases containing four methoxy groups (*the aconines*). The following 'aconi tines' are known:—

Aconitine from *Aconitum Napellus* (Linn.),
*Bikh*aconitine from *Aconitum spicatum* (Stapf.),
*Ind*aconitine from *Aconitum chasmanthus* (Stapf.),
*Jap*aconitine from Japanese aconite roots,
*Pseud*aconitine from *Aconitum deinorrhizum*.

It is probable that Rosendahl's *lappa*conitine, Makoshi's *jes*aconitine, and Dragendorff's *lyc*aconitine, which are all toxic, belong to the group of 'aconitines,' but this cannot be definitely stated until they have been furthe investigated.

The second group contains non-toxic alkaloids typified by atisine and comprises the following:—

Atisine from *Aconitum heterophyllum* (Wall.),
*Palm*atisine from *Aconitum palmatum* (D. Don.).

Aconitine, the principal alkaloid of *Aconitum Napellus* (Linn.), the common monkshood or wolfsbane, in which it occurs along with its decomposition products, benzaconine and aconine, was isolated by Geiger and Hesse (Annalen, 1833, 7, 276), but first obtained in a crystalline state by Groves (Pharm. J. 1860, [ii.] 8, 121). Wright and Luff assigned to it the formula $C_{33}H_{43}O_{12}N$ (Chem. Soc. Trans. 1877, 31, 143; 1878, 33, 151, 318), and later Dunstan and his collaborators (*ibid.* 1891, 59, 271; 1892, 61, 385) adopted for it the formula $C_{33}H_{45}O_{12}N$, a slight modification of that used by Wright and Luff (*l.c.*). Until now almost all the work on crystallised aconitine had been done on alkaloid prepared from the roots of *Aconitum Napellus* grown in England. In 1894 analyses of the crystallised aconitine of commerce, probably from roots of *Aconitum Napellus* grown in Germany, were made by Freund and Beck, who assigned to the alkaloid the formula $C_{34}H_{47}O_{11}N$ (Ber. 1894, 27, 433), and their results were confirmed by Schulze (Arch. Pharm. 1906, 244, 167), who preferred the formula $C_{34}H_{45}O_{11}N$.

There are certain slight but well-marked differences in physical constants between aconitine and its derivatives from English aconite roots, as investigated by Dunstan and his predecessors in England, and those from German aconite roots, which make it probable that the two are distinct. These differences are summarised on p. 631.

Schulze has asserted that the alkaloid from German roots must be identical with that from English roots, since the two are crystallographically identical (*l.c.* 169), but it is known that identity of crystalline form is not always a

Source of alkaloid	Aconitine					Benzaconine	
	Composition	M.p.	$[\alpha]_D$	B·HBr, m.p.	$B{\cdot}HAuCl_4$, m.p.	B·HCl, m.p.	B·HBr, m.p.
English roots	$C_{33}H_{45}O_{12}N$	188·5°	+10·47 to 11·1 in alcohol	163°	Three forms α=135·5° β=152·0° γ=176°	268°	282°
German roots	$C_{34}H_{45}O_{11}N$	196°–197°	+12° 32′	163° 206° (anhydrous)	Two forms α=136° β=149°–152°	Two forms α=217° β=268°	273°

guarantee of identity of composition. Indaconitine is almost precisely similar in crystalline form to aconitine (Dunstan and Andrews, Chem. Soc. Trans. 1905, 87, 1622), although there can be no doubt that these two alkaloids are chemically distinct.

The aconitine of commerce of the present day is best represented by Schulze's formula $C_{34}H_{45}O_{11}N$.

Preparation. The finely-powdered root is exhausted with amyl alcohol mixed with three times its volume of wood spirit. From this extract the wood spirit is distilled under reduced pressure, leaving the whole of the alkaloids dissolved in the residue of amyl alcohol from which they are removed by agitation with dilute (1 p.c.) sulphuric acid. This acid aqueous liquid is shaken with ether to remove ether-soluble, non-basic substances, then made alkaline with dilute ammonia and the liberated alkaloids extracted with ether. The aconine remains dissolved in the water, the aconitine with some benzaconine passing into the ether. The ethereal solution is washed with a small quantity of water and evaporated. The residue is converted into hydrobromide by dissolving it in dilute hydrobromic acid, care being taken to avoid excess of acid. The exactly neutral liquid is evaporated to a small volume and allowed to crystallise. The aconitine hydrobromide is recrystallised until of constant melting-point, and then is converted into the alkaloid by the addition of a slight excess of ammonia to its aqueous solution, the alkaloid being extracted by ether in the usual way. The washed ethereal solution is dried by agitation with fused calcium chloride and evaporated. The small crystals, which are deposited as the ether evaporates, may be recrystallised from dry alcohol by the addition of ether.

Properties. Colourless, anhydrous hexagonal prisms, belonging to the rhombic system (Chem. Soc. Trans. 1891, 59, 288; Ber. 1894, 27, 722; Arch. Pharm. 1906, 244, 169). Easily soluble in chloroform or benzene, less readily in absolute alcohol or ether, very slightly soluble in water, almost insoluble in light petroleum. The aqueous solution is alkaline to litmus; m.p. 196°–197°. Dextrorotatory; in alcoholic solution $[\alpha]_D = +12° 32'$. Salts lævorotatory.

Aconitine is a most powerful poison (Cash and Dunstan, Phil. Trans. 1898, 190, 239). Between $\frac{1}{70}$ and $\frac{1}{50}$ of a grain has been recorded as a fatal human dose.

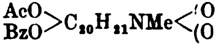
The ordinary salts of aconitine crystallise well. The hydrobromide $B{\cdot}HBr,2\frac{1}{2}H_2O$ is lævorotatory, $[\alpha]_D = -30{\cdot}47°$; m.p. 163° or 206° (anhydrous). The hydriodide, m.p. 226°, is crystalline, and sparingly soluble in water. The aurichloride $B{\cdot}HAuCl_4$ is thrown down as a pale-yellow amorphous precipitate from solutions of the hydrochloride and auric chloride. It crystallises from alcohol with $3H_2O$ and then melts at 135·5°; the anhydrous salt has m.p. 152° (Freund, Ber. 1894, 27, 724).

Reactions. When aconitine is heated at its melting-point it loses 1 mol. of acetic acid and furnishes a new alkaloid *pyraconitine*, and this, on hydrolysis with water or acids, furnishes 1 mol. of benzoic acid and a new base *pyraconine*.

When a salt of aconitine is heated with water, a molecule of acetic acid is split off and the alkaloid *benzaconine*, which also occurs in aconite roots, and has been variously known as *picraconitine*, *isaconitine*, *napelline*, &c., is formed. Benzaconine, in turn, by hydrolysis with alkalis or acids, furnishes 1 mol. of benzoic acid, and the alkaloid *aconine*, which is the final basic product of the hydrolysis. Aconitine is therefore *acetylbenzoylaconine*.

On treatment with acetyl chloride aconitine furnishes a triacetyl derivative (m.p. 207°–208°). When heated with hydriodic acid it yields four mols. of methyl iodide, and must therefore contain four methoxyl groups. It also contains a methyl group linked to nitrogen. On oxidation with acid permanganate aconitine yields acetaldehyde and *oxonitine* $C_{23}H_{29}O_9N$ (Carr, Chem. Soc. Trans. 1912, 101, 3241).

It is probable from the foregoing summary of the chief reactions of aconitine that it may be regarded as derived from a parent base $C_{21}H_{34}N$.



$$\begin{matrix}AcO\\BzO\end{matrix}\!>C_{20}H_{21}NMe<\!\begin{matrix}(OH)_3\\(OMe)_4\end{matrix}$$

Aconitine.

Detection and estimation. The identification of the alkaloid is best accomplished by the determination of the physical constants of its characteristic derivatives, but where minute quantities only are available the characteristic precipitate given with potassium permanganate (Dunstan and Carr, Pharm. J. 1896, [iv.] 2, 122), and the peculiar tingling sensation produced when even very dilute (1 in 4000) solutions of aconitine are applied to the tip of the tongue may be utilised, but these reactions are equally applicable to the 'aconitines' as a class. Various methods for the estimation of aconitine in aconite roots have been proposed, but, as a rule, these estimate some benzaconine and aconine as well as aconitine, and are useless as methods of determining the medicinal value of the roots, since this depends essentially on the amount of aconitine present. Aconitine itself may be estimated by hydrolysing it and determining the amount of acetic acid formed, but this method cannot be used for the estimation of aconitine in the plant since the latter contains other substances which yield acetic acid (Dunstan and Tickle, Pharm. J. 1896, [iv.] 2, 126).

BENZACONINE $C_{32}H_{43}O_{10}N$ has also been called *isaconitine*, *picraconitine*, and *napelline* by various observers. It occurs with aconitine in aconite roots, and may be isolated from the mother liquors from which aconitine hydrobromide has been crystallised, and is also produced by heating an aqueous solution of an aconitine salt in a closed tube.

Properties. Amorphous, dextrorotatory base furnishing crystalline, lævorotatory salts. The hydrobromide crystallises in prisms, m.p. 273° (Schulze, *l.c.*); the hydrochloride occurs in two forms, m.p. 217° and 268° (Freund and Beck, Ber. 1894, 27, 729); the hydriodide has m.p. 204°–205°. The aurichloride has m.p. 135°. According to Schulze (*l.c.*) the tetracetyl derivative of benzaconine is identical with triacetylaconitine.

With the removal of the acetyl group from aconitine the characteristic toxicity disappears and benzaconine is not toxic in the ordinary sense. In some respects its physiological action is antagonistic to that of aconitine (Cash and Dunstan, Phil. Trans. 1898, 190, 239).

ACONINE $C_{25}H_{39}O_9N$, the ultimate basic product of the hydrolysis of aconitine or benzaconine is amorphous and dextrorotatory, but yields hygroscopic lævorotatory salts. It is readily soluble in water, alcohol, or chloroform, but almost insoluble in ether or light petroleum. The hydrochloride $B \cdot HCl, 2H_2O$ has m.p. 175°–176°, and the hydrobromide $B \cdot HBr, 1\frac{1}{2}H_2O$, m.p. 225°. The aurichloride is amorphous. The base furnishes a crystalline tetracetyl derivative. m.p. 231°–232° (Schulze, *l.c.* 1906, 244, 177). On oxidation with permanganate it furnishes acetaldehyde and an amorphous base, but with chromic acid it yields methylamine and two new bases $(OH)_4C_{20}H_{19}O(OMe)_3NMe$ and $C_{19}H_{20}O_4(OMe)_3(NMe) \cdot CO_2H$, the former an amino alcohol and the latter an amino acid (Schulze, Arch. Pharm. 1908, 246, 281; *cf.* Carr, Proc. Chem. Soc. 1912, 28, 253; Brady, *ibid.* p. 289).

Bikhaconitine $C_{36}H_{51}O_{11}N$. The characteristic alkaloid of *Aconitum spicatum* (Stapf.), the roots of which constitute 'bikh'-aconite of North Western India. It may be extracted from the roots by a slight modification of the process described under aconitine. The alkaloid was isolated and characterised by Dunstan and Andrews (Chem. Soc. Trans. 1905, 87, 1636).

Properties. Separates from ether in button-shaped masses, m.p. 118°–123°, or from alcohol on addition of water in white granules containing $1H_2O$, m.p. 113°–116°. Dextrorotatory ($[\alpha]_D^{20°} = +12 \cdot 21°$ in alcohol). The salts are lævorotatory. The hydrochloride $B \cdot HCl, 5H_2O$, m.p. 159°–161° (anhydrous), crystallises and has $[\alpha]_D - 8 \cdot 86°$ (in water); the hydrobromide $B \cdot HBr, 5H_2O$, m.p. 173°–175° (anhydrous) is crystalline and has $[\alpha]_D - 12 \cdot 42°$; the hydriodide $B \cdot HI, 2\frac{1}{2}H_2O$, m.p. 193°–194° (anhydrous), crystallises in needles, and is sparingly soluble in water; the aurichloride $B \cdot HAuCl_4$ crystallises in canary-yellow needles, m.p. 232°–233°. Like all the 'aconitines' bikhaconitine is highly toxic.

Reactions. Bikhaconitine contains six methoxyl groups. When heated at 180° it loses 1 mol. of acetic acid and forms pyrobikhaconitine (amorphous, giving amorphous salts). It undergoes hydrolysis in two stages, thus—

i. $C_{36}H_{51}O_{11}N + H_2O = C_{34}H_{49}O_{10}N + C_2H_4O_2$
Bikhaconitine. Veratroylbikhaconine. Acetic acid.

ii. $C_{34}H_{49}O_{10}N + H_2O = C_{25}H_{41}O_7N + C_9H_{10}O_4$
Veratroylbikhaconine. Bikhaconine. Veratric acid.

Bikhaconitine, therefore, resembles pseudaconitine (*see* p. 634) in furnishing veratric acid in the second stage of its hydrolysis. The alkaloid is, therefore, acetylveratroylbikhaconine, and may be represented thus—

$$[MeO]_4C_{21}H_{27}ON{<}\begin{matrix}OAc\\OVe\end{matrix}$$

VERATROYLBIKHACONINE $C_{34}H_{49}O_{10}N$, the first basic hydrolytic product of bikhaconitine is amorphous and dextrorotatory ($[\alpha]_D = +29 \cdot 9°$ in alcohol). The hydrochloride and hydrobromide are amorphous, but the hydriodide crystallises in rosettes of needles, m.p. 189°–190°. The nitrate forms rosettes of hexagonal prisms, m.p. 175°–178°. The aurichloride forms orange-yellow rosettes of prismatic crystals, m.p. 145°–148° (anhydrous).

BIKHACONINE $C_{25}H_{41}O_7N$, the final basic product of the hydrolysis of bikhaconitine or veratroylbikhaconine. It is dextrorotatory and amorphous, but unlike the 'aconines' as a class, furnishes well-defined crystalline salts. The hydrochloride occurs in rosettes of crystals, m.p. 125°–130°, the hydrobromide in tetragonal prisms, m.p. 145°–150°, and the aurichloride

$$B \cdot HAuCl_4, 3H_2O$$

in glistening rhombic plates, m.p. 129°–132° (hydrated), or 187°–188° (anhydrous).

Indaconitine $C_{34}H_{47}O_{10}N$ is the characteristic alkaloid of *Aconitum chasmanthum* (Stapf.), a species indigenous to India, where it is known as 'Mohri.' It may be extracted from the roots by the process described under aconitine. The alkaloid was isolated and characterised by Dunstan and Andrews (Chem. Soc. Trans. 1905, 87, 1620).

Properties. Indaconitine crystallises in several characteristic forms, but can be obtained in crystals, which are almost identical in form with those of aconitine (*see* above). It has m.p. 202°–203°, and is dextrorotatory $[\alpha]_D = +18° 17'$. The salts crystallise well and are lævorotatory. The hydrochloride $B \cdot HCl, 3H_2O$, m.p. 166°–171° (anhydrous), $[\alpha]_D = -15° 50'$, forms rosettes of silky needles; the hydrobromide, m.p. 183°–187° (anhydrous), $[\alpha]_D = -17° 16'$, crystallises from water in large hexagonal prisms; the aurichloride $B \cdot HAuCl_4, CHCl_3$, m.p. 147°–152°, forms rosettes of needles from chloroform by addition of ether.

Indaconitine gives a characteristic crystalline precipitate with potassium permanganate, the crystals being smaller and less stable than those given by aconitine. Like aconitine, indaconitine is highly toxic (Cash and Dunstan, Proc. Roy. Soc. 1905, B, 76, 468).

Reactions.—Indaconitine contains four methoxyl groups. On hydrolysis it behaves in a manner analogous to aconitine, yielding in the first stage acetic acid and indbenzaconine, the latter, on further hydrolysis, furnishing benzoic acid and pseudaconine. The latter is also the final basic hydrolytic product of pseudaconitine (p. 634), so that pseudaconitine differs only from indaconitine in containing a veratroyl group in place of a benzoyl group. Indaconitine is therefore acetylbenzoylpseudaconine, and may be represented thus—

$$[\mathrm{MeO}]_4\mathrm{C}_{21}\mathrm{H}_{27}\mathrm{O}_2\mathrm{N}{<}\begin{matrix}\mathrm{OAc}\\ \mathrm{OBz}\end{matrix}$$

INDBENZACONINE (Benzoylpseudaconine)

$$C_{32}H_{45}O_9N,$$

the first basic product of the hydrolysis of indaconitine is amorphous and dextrorotatory, $[\alpha]_D = +33° 35'$, but furnishes well crystallised, lævorotatory salts. The hydrobromide

$$B{\cdot}HBr,2H_2O,$$

m.p. 247° (anhydrous) forms rosettes, the hydrochloride $B{\cdot}HCl$, m.p. 242°–244°, octahedra, and the aurichloride, m.p. 180°–182°, orange rosettes. The aurichloro derivative, m.p. 234°–235°, forms minute colourless crystals. On hydrolysis with alkalis indbenzaconine furnishes benzoic acid and pseudaconine (*see* p. 634). As is the case with aconitine the removal of the acetyl group virtually abolishes the toxicity of indaconitine and indbenzaconine is scarcely poisonous in the ordinary sense (Cash and Dunstan, *l.c.*).

PYROINDACONITINE $C_{32}H_{43}O_8N$ exists in two forms. The α- form is produced when the free base, indaconitine, is heated at its melting-point. It is amorphous, but furnishes a crystalline hydrobromide $B{\cdot}HBr$, m.p. 194°–198°, which, like the alkaloid itself, is dextrorotatory. The aurichloride is amorphous. When indaconitine hydrochloride is heated at its melting-point it furnishes β-pyroindaconitine, which is also amorphous, but yields a crystalline hydrobromide, m.p. 248°–250°.

Japaconitine $C_{34}H_{49}O_{11}N$ is the characteristic alkaloid of Japanese aconite roots of commerce. It may be prepared from this source by the method described under aconitine. According to Makoshi the roots of true *Aconitum Fischeri* (Reichb.) contain jesaconitine (*see* below), whilst japaconitine is furnished by the roots of a variety grown in Hondo (Arch. Pharm. 1909, 247, 270), which Holmes regards as *A. uncinatum*, var. *japonicum*. Japaconitine has been frequently investigated, and up to 1900 the balance of evidence was in favour of the view that it was identical with aconitine (Mandelin, Arch. Pharm. 1885, 223, 97, 129, 161; Lübbe, Inaug. Diss. Dorp. 1891; and Freund and Beck, Ber. 1894, 27, 720). The dissimilarity of the two alkaloids had already been asserted by Wright and Luff (Chem. Soc. Trans. 1879, 35, 387), and was finally proved by Dunstan and Read (*ibid.* 1900, 77, 45). Their conclusions have been confirmed by Makoshi (*l.c.*).

Properties. Forms rosettes of prismatic needles, m.p. 204·2°, and is crystallographically distinct from aconitine and pseudaconitine. Dextrorotatory ($[\alpha]_D^{18·5} = +23·6°$ in alcohol), but furnishes lævorotatory salts. The hydrochloride $B{\cdot}HCl,3H_2O$, m.p. 149°–150°, $[\alpha]_D = -23·8°$ in water, crystallises from alcohol and ether in rosettes of hexagonal plates; the hydrobromide $B{\cdot}HBr,4H_2O$, m.p. 172°–173°, crystallises similarly; the aurichloride exists in two modifications, the α- form, m.p. 231° is stable and crystallises in opaque, golden-yellow needles; the β- form, m.p. 154°–160°, is unstable and crystallises in yellow prisms. The physiological action of japaconitine is qualitatively identical with that of aconitine than which it is slightly more toxic (Cash and Dunstan, Proc. Roy. Soc. 1902, 68, 379).

Reactions. Japaconitine, unlike aconitine, reacts with methyl iodide to form a crystalline methiodide, and from this methyljapaconitine $C_{34}H_{48}O_{11}N{\cdot}CH_3$, m.p. 206°, rosettes of colourless needles may be obtained. Japaconitine forms a crystalline triacetyl derivative, m.p. 166°, and contains four methoxyl groups. When heated alone it furnishes 1 mol. acetic acid and 1 mol. pyrojapaconitine (*v. infra*). On hydrolysis it also behaves in a manner analogous to aconitine, giving first 1 mol. each of acetic acid and japbenzaconine. The latter may be further hydrolysed to benzoic acid and japaconine. Japaconitine is therefore acetylbenzoyljapaconine, and may be represented thus (D. a. R.)—

$$\begin{matrix}[\mathrm{HO}]_3\\ [\mathrm{OMe}]_4\end{matrix}{>}\mathrm{C}_{21}\mathrm{H}_{\ 4}\mathrm{NH}{<}\begin{matrix}\mathrm{OAc}\\ \mathrm{OBz}\end{matrix}$$

JAPBENZACONINE $C_{32}H_{47}O_{10}N$, the first basic hydrolytic product of japaconitine, also occurs with this alkaloid in Japanese aconite roots. Unlike the analogous benzaconine, it crystallises, though with difficulty, m.p. 183°. Dextrorotatory ($[\alpha]_D = +40·16°$ in alcohol). The salts crystallise well, and are lævorotatory; the hydrochloride $B{\cdot}HCl,H_2O$, m.p. 253°, forms minute rosettes; the aurichloride $B{\cdot}HAuCl_4$ crystallises from alcohol and then melts at 219°. The colourless aurichloro derivative

$$C_{32}H_{46}O_{10}N{\cdot}AuCl_2,$$

m.p. 178°, forms rosettes of needles (D. a. R. *l.c.*).

JAPACONINE $C_{25}H_{41}O_9N$, the final basic product of the hydrolysis of japaconitine or japbenzaconine, is amorphous, and hygroscopic and yields hygroscopic salts, which crystallise with difficulty. Its solutions reduce gold chloride and Fehling's solution. The base is dextrorotatory (D. a. R. *l.c.*).

PYROJAPACONITINE $C_{32}H_{45}O_9N$ is formed by heating japaconitine at its melting-point when 1 mol. of acetic acid is evolved. Crystallises in colourless needles, m.p. 167°–168°, is lævorotatory ($[\alpha]_D = -65·89°$ in alcohol), and furnishes well-crystallised salts; the aurichloride

$$B{\cdot}HAuCl_4,$$

m.p. 160°–161° (from chloroform), or 188°–189° (from alcohol and ether). On hydrolysis by alkalis the base gives rise to 1 mol. benzoic acid and a new base *pyrojapaconine*, which is amorphous, hygroscopic, and lævorotatory, and furnishes amorphous salts.

Jesaconitine $C_{40}H_{51}O_{12}N$, isolated by Makoshi (Arch. Pharm. 1909, 247, 251) from 'Bushi' roots obtained from a species of aconite, *A. Fischeri* (?), found in the island of Hokkaido or Jeso in Japan. It was not obtained crystalline, but a crystalline triacetyl derivative, m.p. 213°, was prepared. On hydrolysis jesaconitine yielded benzoic acid, anisic acid, and aconine, identical with that obtained from aconitine, so that it is regarded as benzoylanisoylaconine. Jesaconitine is highly toxic (Makoshi, *l.c.*).

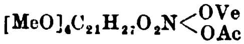
Lappaconitine $C_{34}H_{48}O_8N_2$, obtained by Rosendahl (J. Pharm. Chim. 1896, [vi.] 4, 262) from the roots of *Aconitum septentrionale* (Koelle). It crystallises in hexagonal prisms, m.p. 205°, is dextrorotatory, shows a reddish-violet fluorescence in ether, and furnishes crystalline salts. On hydrolysis it yields two bases; one, m.p. 98°, readily soluble, and the other. m.p. 106°, nearly insoluble in ether; at the same time an acid, m.p. 114°, giving a purple colour with ferric chloride, is produced. Lappaconitine is highly toxic. The roots also contain *cynoctonine* $C_{36}H_{55}O_{12}N_2$ (amorphous, bitter, and much less toxic than lappaconitine) and *septentrionaline* $C_{31}H_{48}O_9N_2$, amorphous, bitter, and about equal in toxicity to cynoctonine (*cf.* Orloff, P. Z. f. R. 1907, 36, 213).

Lycaconitine $C_{36}H_{46}O_{10}N_2$, obtained by Dragendorff and Spohn (P. Z. f. R. 1884, 23, 313) and later by Schulze and Bierling (Arch. Pharm. 1913, 251, 8) along with *myoctonine* ($C_{36}H_{42}O_{10}N_2$) and an unnamed base, from the roots of *Aconitum Lycoctonum* (Linn.), is amorphous and dextrorotatory. On hydrolysis with acids it furnishes anthranoyl-lycoctonine (Dragendorff's lycaconine) and succinic acid. On hydrolysis with sodium hydroxide lycoctonine $C_{25}H_{39}O_7N,H_2O$ and lycoctoninic acid $C_{11}H_{15}O_5N$, both crystalline, are formed. Lycoctonine had been found previously by Hübschmann in the roots (J. 1857, 416; 1866, 483; *cf.* Wright and Luff, Pharm. J. 1878–9, [iii.] 8, 169). All the alkaloids described are heart poisons.

Pseudaconitine $C_{36}H_{51}O_{12}N$. The characteristic alkaloid of *Aconitum deinorrhizum*, the roots of which form Nepaul aconite of commerce. It may be extracted from the roots by the process described under aconitine. Pseudaconitine has been frequently examined (Wright and Luff, Chem. Soc. Trans. 1878, 33, 151; Mandelin, Arch. Pharm. 1884, 222, 97, 129, 161), and most recently by Dunstan and Carr (Chem. Soc. Proc. 1895, 154; and Chem. Soc. Trans. 1897, 71, 350).

Properties. Colourless crystals of rhomboidal shape, m.p. 211°–212° (decomp.); $[\alpha]_D = +18° 36'$ in alcohol. Readily soluble in alcohol, less so in ether, very slightly in water, almost insoluble in light petroleum. The salts are lævorotatory; the hydrobromide $B{\cdot}HBr,2H_2O$, m.p. 191° (anhydrous), and the nitrate $B{\cdot}HNO_3,3H_2O$, m.p. 192°, are crystalline. The hydrochloride is amorphous, but the aurichloride, m.p. 235°–236°, may be crystallised from alcohol. Pseudaconitine exerts a physiological action similar to that of aconitine, but is much more toxic (Cash and Dunstan, Proc. Roy. Soc. 1902, 68, 379).

Reactions. On heating an aqueous solution of a neutral pseudaconitine salt in a closed tube at 135° the alkaloid undergoes hydrolysis, yielding 1 mol. acetic acid and 1 mol. veratroylpseudaconine. The latter is hydrolysed in the cold by sodium hydroxide in alcohol, furnishing 1 mol. of veratric acid and 1 mol. of pseudaconine. When heated at its melting-point pseudaconitine loses 1 mol. acetic acid and furnishes pyropseudaconitine. Pseudaconitine, in view of these reactions, is to be regarded as acetylveratroylpseudaconine



$$[MeO]_4C_{21}H_{27}O_2N<\begin{matrix}OVe\\OAc\end{matrix}$$

No relationship has yet been traced between pseudaconine and aconine (D. a. C.; *cf.* Freund and Niederhofheim, Ber. 1896, 29, 6, 852).

VERATROYLPSEUDACONINE $C_{34}H_{49}O_{11}N$. The first basic product of the hydrolysis of pseudaconitine (*see* above) separates in large, irregularly-shaped crystals from ether, m.p. 199°. readily soluble in chloroform or alcohol, nearly insoluble in water or light petroleum, $[\alpha]_D = -38° 18'$ in alcohol. The salts crystallise well; the hydrobromide $B{\cdot}HBr,3H_2O$ in prisms; the nitrate $B{\cdot}HNO_3$ in rosettes of rhombic prisms, m.p. 222° and 232°; the aurichloride $B{\cdot}HAuCl_4$ is amorphous (D. a. C.). Veratroylpseudaconine is not toxic (Cash and Dunstan, *l.c.*).

PSEUDACONINE $C_{25}H_{41}O_8N$, the ultimate basic product of the hydrolysis of pseudaconitine and indaconitine (p. 632), forms large colourless crystals, m.p. 94°–95°, containing 1 mol. alcohol of crystallisation. Dextrorotatory ($[\alpha]_D = 38° 12'$ in water). The salts are amorphous.

PYROPSEUDACONITINE $C_{34}H_{47}O_{10}N$. Formed by heating pseudaconitine at its melting-point, when 1 mol. acetic acid is evolved; it is amorphous, but yields a hydriodide, crystallising in prisms (D. a. C. *l.c.*).

Atisine $C_{22}H_{31}O_2N$, the characteristic alkaloid of *Aconitum heterophyllum* (Wall.) of Northern India. It was first isolated by Broughton in 1873, and was subsequently examined by Wasowicz (Arch. Pharm. 1879, 214, 193), Wright (Year Book Pharm. 1879, 422), and later by Jowett (Chem. Soc. Trans. 1896, 69, 1518). Atisine is amorphous, readily soluble in water, alcohol, ether, or chloroform, lævorotatory ($[\alpha]_D^{19°} = -19{\cdot}6°$ in alcohol). It yields crystalline, dextrorotatory salts; $B{\cdot}HCl$, prisms, m.p. 296° (decomp.); $B{\cdot}HI$, tablets, m.p. 279°–281° (decomp.); $B_2{\cdot}H_2PtCl_6$, crystalline yellow powder, m.p. 229° (decomp.). When heated with water in a closed tube atisine furnishes a *hydrate* $C_{22}H_{33}O_3N$, which is amorphous, and yields amorphous salts. Atisine is non-toxic (Jowett, *l.c.*).

Palmatisine. A colourless, crystalline, non-toxic alkaloid, m.p. 285°, found in the roots of *Aconitum palmatum* (D. Don.), a species indigenous to India (Dunstan and Carr).

Adenine. *See* under *Caffeine* (p. 642).

Adlumine $C_{39}H_{41}O_{12}N$, crystals, m.p. 188°, occurs in *Adlumia cirrhosa* (Rafin.) with *adlumidine* $C_{30}H_{29}O_9N$, plates, m.p. 234°, protopine (p. 665), and β-homochelidonine (p. 645) (Schlotterbeck and Watkins, Ph. Ar. 1903, 6, 17).

Agmatine. *See* p. 653.

Alstonine. One of a series of ill-defined alkaloids occurring in *Alstonia* spp. (Hesse, Annalen, 1880, 203, 147; 205, 360), including *alstonamine*, *alstonidine*, *ditaine*, *ditamine*, &c.

Angeline $C_{10}H_{13}O_3N$ (surinamine, geoffroyine, andirine, rhatanine) is a methyltyrosine (Hiller-Bombien, Arch. Pharm. 1892, 230, 513; Goldschmidt, Monatsh. 1913, 33, 1379; 34, 659), widely distributed in plants.

Anhalonamine, Anhalonidine, and **Anhalonine.** *See* under *Mezcaline* (p. 656).

Aporeine. *See* under *Rheadine* (p. 674).

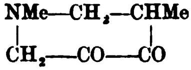
Arachine $C_5H_{14}ON_2$, an alkaloid occurring with choline and betäine in earth-nut (ground-nut, monkey-nut) meal (*Arachis hypogea* (Linn.)). Syrup; the aurichloride and platinichloride are crystalline. Produces somnolence in frogs and rabbits (Mooser, Landw. Versuch-Stat. 1904, 60, 321).

ARECOLINE AND THE ALKALOIDS OF ARECA NUTS.

Arecoline $C_8H_{13}O_2N$ is the chief alkaloid of areca nuts (*Areca Catechu* (Linn.)). It is a strongly alkaline liquid, b.p. 220°, which furnishes crystalline salts. On hydrolysis by alkalis or acids it gives methyl alcohol and arecaïdine (*v. infra*). Arecoline is highly toxic (Meier, Biochem. Zeitsch. 1907, 2, 415).

Arecaïdine $C_7H_{11}O_2N,H_2O$ occurs in areca nuts, and is produced by the hydrolysis of arecoline. It is crystalline, m.p. 222°–223°, yields a crystalline aurichloride, and is non-toxic. In constitution arecaïdine is N-methyl-Δ^3-tetrahydronicotinic acid, and has been synthesised by Jahns (*see* below).

Arecaine $C_7H_{11}O_2N,H_2O$, the third alkaloid of areca nuts, is isomeric with arecaïdine. It is crystalline, m.p. 213° (decomp.), neutral, and gives crystalline salts. It has the following constitution :—



$$\begin{array}{ccccc} NMe & - & CH_2 & - & CHMe \\ | & & & & | \\ CH_2 & - & CO & - & CO \end{array}$$

Arecaine.

Guvacine $C_6H_9O_2N$, the fourth alkaloid of areca nuts, is crystalline, m.p. 271°–272° (decomp.), and neutral in reaction. On methylation it furnishes arecaine in part, whence the latter is regarded as the N-methyl derivative of guvacine.

Our knowledge of the areca-nut alkaloids is chiefly due to Jahns (Ber. 1888, 21, 3404; 1890, 23, 2972; 1891, 24, 2615; Arch. Pharm. 1892, 229, 669; *cf.* Willstätter, Ber. 1897, 30, 729; and Meyer, Monatsh. 1902, 23, 22; Wohl and Johnson, Ber. 1907, 40, 4712).

Arginine $C_6H_{14}O_2N_4$ is α-amino-δ-guanino-*n*-valeric acid (Sörensen, Ber. 1910, 43, 643). Occurs frequently in etiolated embryos of plants (Schulze and others, *ibid.* 1886, 19, 1177; 1891, 24, 1098, 2701; 1897, 30, 2880; 1899, 32, 3191; Ellinger, *ibid.* 1898, 31, 3183; 1899, 32, 3542) (*v.* Vol. I. p. 289).

Aricine $C_{23}H_{26}O_4N_2$ is an alkaloid found in cusco and cuprea barks derived from plants closely allied to the cinchonas. Crystals, m.p. 188°; lævorotatory $[\alpha]_D = -58{\cdot}18°$ in alcohol. The salts are crystalline and dextrorotatory (Hesse, Annalen, 1877, 185, 320; Moissan and Landrin, Compt. rend. 1890, 110, 469).

Aristinic acid $C_{18}H_{13}O_7N$, greenish-yellow needles, m.p. 275° (decomp.). Occurs with *aristidinic acid* $C_{19}H_{13}O_7N$, and *aristolic acid* $C_{15}H_{11}O_7N$, in *Aristolochia argentina* (Griseb.) (Hesse, Arch. Pharm. 1895, 233, 684).

Aristolochine $C_{32}H_{22}O_{13}N_2$, orange-yellow needles, decomposing at 215°. Occurs in *Aristolochia Clematitis* (Linn.) and *A. rotunda* (Linn.). It is a weakly acid base (Pohl, Arch. expt. Path. Pharm. 1891, 29, 282). According to Hesse (Arch. Pharm. 1895, 233, 684) aristolochine has the formula $C_{17}H_{11}O_7N$ and is a homologue of aristolic acid (*see* under *Aristinic acid*). The alkaloid is highly toxic.

Aspidospermine $C_{22}H_{30}ON_2$ and **aspidospermatine** $C_{22}H_{28}O_2N_2$ are two of a number of alkaloids found in quebracho bark (*Aspidosperma Quebracho* (Schlecht.)) (Fraude, Ber. 1878, 11, 2190; 1879, 12, 1560; Hesse, Annalen, 1882, 211, 249).

Atisine. *See* under *Aconitine* (p. 634).

Atropamine. *See* under *Atropine* (p. 637).

Atroscine. *See Scopolamine*, under *Atropine* (p. 639).

ATROPINE AND THE SOLANACEOUS ALKALOIDS.

This group comprises the following members, and possibly others not yet fully examined :—

Atropine and hyoscyamine $C_{17}H_{23}O_3N$;
*nor*Hyoscyamine $C_{16}H_{21}O_3N$;
Apoatropine and belladonnine $C_{17}H_{21}O_2N$;
Tropacocaine $C_{15}H_{19}O_2N$ (*see* p. 647) ;
Scopolamine $C_{17}H_{21}O_4N$;
Meteloidine $C_{13}H_{21}O_4N$.

These are all tertiary bases except *nor*-hyoscyamine, and on hydrolysis furnish an acid and an amino alcohol. Of the eight alkaloids only three are of importance in medicine, viz. atropine, hyoscyamine, and scopolamine. The best known sources of the three alkaloids are belladonna (*Atropa Belladonna* (Linn.)), henbane (*Hyoscyamus niger* (Linn.)), and stramonium (*Datura Stramonium* (Linn.)), all of which are used in medicine. Other plants which contain them in important quantities, and either are or may be used commercially as sources of the alkaloids, are *Hyoscyamus muticus* (Linn.), *H. albus* (Linn.), and *H. reticulatus* (Linn.), *Datura Metel* (Linn.), *D. arborea* (Linn.), *D. quercifolia* (H. B. and K.), *Duboisia myoporoides* (R.Br.), *Scopolia carniolica* (Jacq.), and *S. japonica* (Maxim.) and *Mandragora officinarum* (Linn.). As a rule, at least two of the alkaloids, usually hyoscyamine and scopolamine, are found together in each plant, but *H. muticus* is remarkable in containing hyoscyamine without any admixture of atropine or scopolamine. It is probable that atropine rarely, if ever, occurs pre-formed in plants, and the traces generally found in the extracted alkaloids are due to isomerisation of hyoscyamine either by drying the plant or by the action of chemical agents used for extraction. In general, the alkaloids are present in the stem, leaves, root, and seed, and the amount of total alkaloid present in each of these parts shows great variation with the time of collection and the climatic conditions under which the plant was grown.

Preparation. The method used for the extraction of these alkaloids varies to some extent with the material employed, but the following general process gives good results as a rule. The finely-ground, air-dry drug is exhausted by percolation with cold 90 p.c. alcohol. and the greater part of the solvent removed by distillation under reduced pressure. In the case of seeds, percolation with alcohol should be preceded by percolation with light petroleum to remove oil. The semi-solid extract is then treated with dilute (0·5 p.c.) hydrochloric or sulphuric acid, until no more alkaloid is removed. This acid liquid is filtered, shaken with small quantities of chloroform, if necessary, to remove traces of chlorophyll, oil, or other soluble non-basic matters, then made slightly alkaline with dilute ammonia, and the alkaloid extracted by means of chloroform. The latter is distilled off, leaving, as a rule, a clean gum-like residue. From this, by solution in chloroform and careful addition of light petroleum, hyoscyamine may be caused to separate in crystalline form. If scopolamine is present it remains dissolved in the chloroform, and may be caused to separate by further addition of light petroleum. The alkaloids may be purified by re-crystallisation from alcohol by addition of water, when hyoscyamine separates first. The best source of hyoscyamine is the Egyptian plant, *Hyoscyamus muticus*, since this contains no scopolamine.

ESTIMATION OF TOTAL ALKALOIDS. Dunstan and Ransom have devised the following methods:

For the root. Exhaust by hot percolation 20 grms. of the finely-powdered root with a mixture of equal parts of chloroform and absolute alcohol, which readily dissolves the alkaloidal salts. Agitate the solution with 25 c.c. of water, when the salts pass into the aqueous layer, and the resin, fat, colouring matter, &c., remain dissolved in the chloroform. Repeat this extraction with water. Wash the 50 c.c. of water with a little pure chloroform to remove adhering impurity, then add ammonia in slight excess, and dissolve out the liberated alkaloids by agitation with chloroform in the usual way. The residue of alkaloid left on the evaporation of the chloroform is dried at 100° and weighed (Pharm. J. 1883–4, [iii.] 14, 623).

For the leaves. 20 grms. of the finely-powdered dry leaves are exhausted with absolute alcohol. The liquid is largely diluted with water, acidified with hydrochloric acid, and repeatedly extracted by agitation with chloroform until the whole of the chlorophyll, fat, &c., has been removed. The liquid is then made alkaline with ammonia, and extracted with chloroform, which, on evaporation, leaves a residue of alkaloid. This must be dried at 100° before being weighed. This process answers equally well for stems or fruit capsules, and for seeds, if the latter are first extracted with light petroleum to remove oil (Pharm. J. 1885–6, [iii.] 16, 237).

Extract of the leaves. From 1 to 2 grms. of the extract are dissolved, as far as possible, in warm dilute hydrochloric acid, any residue being extracted with the dilute acid until all the alkaloid has been dissolved. The acid liquid is then extracted with chloroform until nothing further is removed, and, after this treatment, is made alkaline with ammonia, and the free alkaloid removed by agitating again with chloroform, which on evaporation leaves a residue of alkaloid that is dried at 100°C. and weighed (*ibid.* 1885–6, [iii.] 16, 238).

Alcoholic extract of the root. 2 grms. of this extract are dissolved as far as possible in dilute hydrochloric acid. This solution is then treated as described under the leaf extract (*ibid.* 1885–6, [iii.] 16, 777).

No method is yet available for the quantitative separation and estimation in mixtures of the individual mydriatic alkaloids, but the approximate amounts of each present may sometimes be determined by careful fractionation with gold chloride.

Atropine $C_{17}H_{23}O_3N$ was first obtained by Mein (Annalen, 1833, 6, 67) from the root of *Datura Stramonium* (Linn.), and called by him *daturine*. Geiger and Hesse obtained it independently (*ibid.* 1833, 5, 43; 6, 44; 7, 269) from belladonna root, and their material was analysed by Liebig, who assigned to it the empirical formula now in use. Atropine is stated to occur with hyoscyamine and a little scopolamine in belladonna and stramonium and with more scopolamine in *Scopolia japonica* (Maxim), but there is reason to believe that the alkaloid does not exist pre-formed in plants, although it may be produced in the course of preparation by the action of alkalis on hyoscyamine. In any case, the commercial alkaloid is now obtained invariably by conversion of hyoscyamine by the action of very dilute alkali (Will and Bredig, Ber. 1888, 21, 2797; *cf.* Gadamer, Arch. Pharm. 1901, 239, 294).

Properties. Prismatic crystals, m.p. 115·5°. Readily soluble in alcohol or chloroform, less soluble in ether or hot water, sparingly soluble in cold water. The aqueous solution is alkaline to litmus, and has a very bitter taste. Atropine is optically inactive. It is slightly volatile with steam (Dragendorff). One of the most remarkable properties of atropine is that of causing dilation of the pupil of the eye, a property which is often made use of in detecting it and other alkaloids of this group, several of which exert this mydriatic action. A drop or two of an aqueous solution, containing 1 part of atropine in 130,000 parts of water, when introduced into the eye of a cat is sufficient to produce this effect. When taken internally atropine is highly poisonous; some of the alkaloid is apparently excreted unchanged in the urine.

The ordinary salts of atropine are crystalline and soluble in water. The sulphate

$$B_2 \cdot H_2SO_4, H_2O$$

is commonly used in medicine; it forms colourless needles, m.p. 187°–188°, 194° (dry). The aurichloride $B \cdot HAuCl_4$ appears as an oily precipitate when produced in the ordinary manner. This soon solidifies to a crystalline mass, which may be re-crystallised from water, acidified with hydrochloric acid. The crystals melt at 135° (Ladenburg, Annalen, 1880, 206, 274); near 138° (Hesse, *ibid.* 1892, 271, 100). This salt and the picrate, m.p. 175°–176°, are useful for the identification of the alkaloid, since the corresponding salts of the other alkaloids of this group melt at different temperatures.

Reactions and constitution. Among the characteristic qualitative reactions of atropine may be mentioned the production of an odour of heliotrope or of bitter almond oil, when a solution of the alkaloid is warmed with sulphuric acid and a fragment of potassium dichromate or permanganate. When the alkaloid is evaporated to dryness with a few drops of fuming nitric acid a residue is obtained which turns violet (changing to red) when it is moistened with alcoholic potash (Vitali, Zeitsch. anal. Chem. 1881, 20, 563). Other characteristic colour reactions are described by Reichard (Chem. Zeit. 1904, 28, 1048). Many alkaloids form white, insoluble compounds with mercuric chloride, but when a solution of this salt is added to a dilute alcoholic solution of atropine (not a salt) and the mixture is warmed, a yellowish-red precipitate of mercuric oxide is thrown down, and after a time a colourless crystalline double salt separates from the solution (Gerrard, Pharm. J. 1883–4, [iii.] 14, 718).

Atropine yields an anhydride (*apoatropine*) (*see* below) when heated with dilute nitric acid (Pesci, Gazz. chim. ital. 1881, 11, 538; 1882, 12, 60), which Hesse subsequently isolated from belladonna root and named atropamine (Annalen, 1892 271 124; *cf.* Merck, Zeitsch. anal. Chem.

1892, 31, 229; and Hesse, Annalen, 1893, 277, 290). Apoatropine is not mydriatic. Atropine readily undergoes hydrolysis when warmed with alkalis or strong acids. By heating it with concentrated hydrochloric acid in a closed tube at 130°, or with baryta water at 60°, it is completely resolved into *tropine* $C_8H_{15}ON$, and *tropic acid* (α-phenyl-β-hydroxypropionic acid)

$$CH_2(OH)\cdot CH(C_6H_5)COOH$$

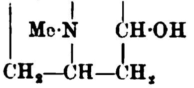
$$C_{17}H_{23}O_3N+H_2O=C_8H_{15}ON+C_9H_{10}O_3$$

Atropine. Tropine. Tropic acid.

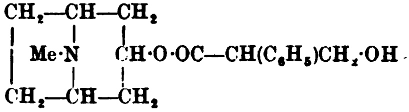
At higher temperatures than these, or after prolonged heating, the tropic acid suffers dehydration, forming, when alkalis are used, atropic acid $CH_2:C(C_6H_5)COOH$.

TROPINE $C_8H_{15}ON$ forms large, colourless tablets, m.p. 63°; b.p. 229°; sp.gr. 1·0392 at 76°/4°, soluble in water, alcohol, or ether. It is a strong base, which forms crystalline salts. It is poisonous, but does not dilate the pupil of the eye. Tropine and tropic acid unite to form tropine tropate $C_8H_{15}NO\cdot C_9H_{10}O_3$, and this salt, when heated with dilute hydrochloric acid, loses water and furnishes atropine, identical with the natural alkaloid (Ladenburg, Annalen, 1883, 217, 74). Similarly, by heating other organic salts of tropine with dilute hydrochloric acid, dehydration occurs, with production of the acyl derivative of tropine. The bases thus formed have been called by Ladenburg *tropeïnes.* In this way *l*-atropine (*l*-tropyltropeine), *d*-atropine (*d*-tropyltropeine), *pseudo*atropine (atrolactyltropeine), and atropamine (apoatropine, atropyltropeïne) have been prepared (*cf.* Wolffenstein and Mamlock, Ber. 1908, 41, 723; and Wolffenstein and Rolle, *ibid.* 1908, 41, 733). Several of the tropeines exert a mydriatic action. *Phenylglycollytropeine* $C_{16}H_{21}O_3N$ has been used in medicine under the name *homatropine.* Its mydriatic effect is less persistent than that of atropine. As a result of Ladenburg's work it has been generally assumed that only those tropëines produce a mydriatic effect which contain an alcoholic (not phenolic) hydroxyl in the aromatic acid residue, thus acetyl-, benzoyl-, and salicyl-tropeines are not mydriatic, whilst mandelyltropeine is mydriatic. Jowett and Pyman find that this is not strictly true, mydriasis being produced by terebyltropeine (Chem. Soc. Trans. 1906, 89, 360), and only slightly by *o*-carboxyphenylglyceryltropeine (*ibid.* 1907, 91, 93; 1909, 95, 1020; and Proc. Int. Cong. Appl. Chem. 1909) which should be very active. Certain tropeines containing a lactone group become less active when the lactonic grouping is opened by the action of alkali.

Tropine has been the subject of numerous investigations especially by Ladenburg, Merling and Willstätter culminating in its synthesis by the last-named from suberone as a starting-point (Ber. 1901, 34, 3163; Annalen, 1903, 326, 23). On the basis of these results tropine and atropine are now generally represented by the following formulæ—



Tropine.



Atropine (tropyltropeïne).

Tropine undergoes a series of interesting decompositions under the action of various reagents. The most interesting of these are as follows: When heated with dehydrating agents it furnishes *tropidine* $C_8H_{13}N$ (Ladenburg, Annalen, 1883, 217, 177), a strongly alkaline oil, b.p. 162°–163°, sp.gr. 0·9467 at 19°/4°, which has an odour recalling that of coniine. On oxidation with chromic acid tropine yields in turn *tropinone* $C_8H_{13}ON$ (Willstätter, Ber. 1896, 29, 396), m.p. 41°–42°, b.p. 224°–225°, *tropinic acid* $C_8H_{13}O_4N$ (Merling, Annalen, 1883, 216, 348; Willstätter, *l.c.*), and finally *ecgoninic acid* $C_7H_{11}O_3N$ (*see* under *Cocaine*), which was shown by Willstätter and Bode to be N-methylpyrrolidine-2-acetic acid (Ber. 1901, 34, 519), thus proving the presence of a pyrrolidine ring in tropine. For a detailed account of the important researches in the tropine series, Schmidt's Über die Erforschung der Konstitution und die Versuche zur Synthese wichtiger Pflanzenalkaloide, i. 1900; ii. 1904 (Enke, Stuttgart), should be consulted.

Apoatropine (*Atropamine*) $C_{17}H_{21}O_2N$. This base was first prepared by Pesci (Gazz. chim. ital. 1881, 11, 538; 1882, 12, 60) by the action of nitric acid on atropine, and was subsequently isolated by Hesse from belladonna under the name atropamine, the identity of the two bases being established by Merck (Arch. Pharm. 1891, 229, 134; 1893, 231, 110; *cf.* Hesse, Annalen, 1891, 261, 87; 1893, 277, 290). It is also formed by the action of cold sulphuric acid on atropine or hyoscyamine, and may be isolated by pouring the solution into water immediately. By prolonged action of the acid apoatropine is converted into belladonnine (*v. infra*). Apoatropine crystallises in prisms, m.p. 60°, and furnishes crystalline salts; the hydrochloride B·HCl, m.p. 237°–239°, forms leaflets, and the aurichloride $B\cdot HAuCl_4$, needles, m.p. 110°–112°. On hydrolysis with baryta water it furnishes tropine and atropic acid, and it has been synthesised by Ladenburg from these two substances and called atropyltropëine (Annalen, 1883, 217, 102).

Belladonnine $C_{17}H_{21}O_2N$. This alkaloid is stated to occur in the leaves and root of *Atropa Belladonna* (Linn.) (Hübschmann, J. 1858, 376; Kraut, Ber. 1880, 13, 165; Dürkopf, *ibid.* 1889, 22, 3183; Hesse, Annalen, 1891, 262, 100). According to Merling (Ber. 1884, 17, 381) it has the formula $C_{17}H_{21}O_2N$, and is isomeric with anhydro-atropine (apoatropine), and this was confirmed by Hesse (*l.c.* 1892, 271, 123; 1893, 277, 295), who stated that it can be prepared by the action of (1) sulphuric acid on atropine or hyoscyamine, or (2) hydrochloric acid on atropamine (apoatropine). Belladonnine is a resinous, uncrystallisable base, which is hydrolysed with much greater difficulty than the other solanaceous alkaloids, yielding tropine $C_8H_{15}ON$ and atropic acid (Merling). It appears to be devoid of mydriatic power.

Hyoscyamine $C_{17}H_{23}O_3N$. An isomeride of atropine. It is the most common of the solanaceous alkaloids, being the principal alkaloid in *Atropa Belladonna* (Linn.) (Schmidt, Arch. Pharm. 1905, 243, 303), *Hyoscyamus niger* (Linn.), and *H. albus* (Linn.), the sole mydriatic alkaloid in *H. muticus* (Linn.) (Dunstan and Brown, Chem. Soc. Trans. 1899, 75, 74; 1901, 79, 72), and the chief alkaloid in *Datura Stramonium* (Linn.), *Duboisia myoporoides* (R. Br.), *Scopolia carniolica* (Jacq.) (Dunstan and Chaston, Pharm. J. 1889–1890, [iii.] 20, 461), and *S. japonica* (Maxim.) (Schmidt, Arch. Pharm. 1888, [iii.] 26, 185, 214), and in other similar plants; it exists in minute quantities in lettuce, *Lactuca virosa* (Linn.) and *L. Scariola* (Linn.) (Dymond, Chem. Soc. Trans. 1892, 61, 90).

Preparation. Hyoscyamine may be extracted from the various plants containing it by means of the process described in the introduction to this section. The best source of the alkaloid is the stem and leaves of *Hyoscyamus muticus*, since this material is free from other mydriatic alkaloids of this group. It may also be obtained from henbane or stramonium. In preparing the alkaloid great care must be taken not to leave it in contact with alkalis, since these readily convert it into atropine. Hyoscyamine is but little used in medicine, and is generally used merely as a source of atropine. When atropine and scopolamine are also present in the plant these alkaloids are obtained with the hyoscyamine. The isolation of pure hyoscyamine from the mixture of the alkaloids is a difficult operation. The greater part of the atropine may be removed by repeated crystallisation from dilute alcohol, the hyoscyamine for the most part remaining dissolved. The isolation of pure hyoscyamine can only be certainly accomplished by converting the alkaloid into the aurichloride and repeatedly crystallising this salt from dilute hydrochloric acid until it melts at the proper temperature. The alkaloid may be regenerated from the aurichloride by decomposing it with hydrogen sulphide in the usual manner.

Properties. Long, silky crystals, m.p. 108·5°; lævorotatory $[\alpha]_D = -14{\cdot}5°$ (Ladenburg, Annalen, 1880, 206, 274); $[\alpha]_D = -20{\cdot}97°$ (Will, Ber. 1888, 21, 1717); $[\alpha]_D = -20{\cdot}3°$ (Hesse, Annalen, 1892, 271, 100); $[\alpha]_D = -22{\cdot}06°$ (in alcohol) Carr and Reynolds (Chem. Soc. Trans. 1910, 97, 1331). Readily soluble in benzene, chloroform, or alcohol, less readily in ether or cold water. When heated the alkaloid sublimes, with partial decomposition, and it is said to be slightly volatile with steam. When hyoscyamine is heated to a temperature slightly higher than its melting-point, it is converted into atropine (Schmidt, Ber. 1888, 21, 1829). This conversion also takes place with great facility when hyoscyamine is warmed or even allowed to stand in the cold, with caustic alkalis or alkali carbonates, but it only takes place extremely slowly in presence of ammonia (Will, Ber. 1888, 21, 1717, 2777). Hyoscyamine exerts a strong mydriatic action, and is a powerful poison.

Many of the ordinary salts of hyoscyamine are crystalline and soluble in water. The sulphate $B_2{\cdot}H_2SO_4$, crystallises well from alcohol and melts at 206°. The aurichloride $B{\cdot}HAuCl_4$ is best crystallised from dilute hydrochloric acid. It melts at 159°–160° (Ladenburg, *l.c.*); 162° (Will, *l.c.*); 159° (Hesse, *l.c.*); but, unlike atropine aurichloride, it does not melt when heated under water. This salt is less soluble in acidified water than atropine aurichloride, from which it may be separated by repeated crystallisation.

Reactions. The qualitative reactions of hyoscyamine are, for the most part, identical with those of atropine. When heated with acids or alkalis, like atropine, it undergoes hydrolysis into *tropine* and *tropic acid.* On reversing this reaction by heating together the tropine and tropic acid, atropine and not hyoscyamine is formed. According to Gadamer (Arch. Pharm. 1901, 239, 294) hyoscyamine is, in the first place, converted by alkalis into atropine, and it is really this alkaloid which is hydrolysed. The same author states that by the action of water at atmospheric temperature hyoscyamine is resolved into *r*-tropine and *l*-tropic acid, and consequently hyoscyamine must be *l*-tropyl-*r*-tropine; Amenomiya (*ibid.* 1902, 240, 498) has synthesised *l*-hyoscyamine and *d*-hyoscyamine. Ladenburg and Hundt's *d*- and *l*-atropines (Ber. 1889, 22, 2590) are regarded as mixtures of *d*- and *l*-hyoscyamine with atropine.

Detection. Hyoscyamine may be detected by its mydriatic action and by most of the reactions described under atropine. Its partial separation from atropine may be effected by recrystallisation from dilute alcohol, but it can only be completely separated and identified by preparing its aurichloride, which is characterised by its melting-point (for details *see* Dunstan and Chaston, Pharm. J. 1889–1890, [iii.] 20, 461).

Mandragorine was obtained by Ahrens (Ber. 1889, 22, 2159) from *Mandragora officinarum* (Linn.), and from the same source by Hesse (J. pr. Chem. 1901, [iii.] 64, 274), along with hyoscyamine, scopolamine, and pseudohyoscyamine. According to Thoms and Wentzel (Ber. 1901, 34, 1023), Ahrens' mandragorine is merely a mixture of hyoscyamine with scopolamine and possibly a third alkaloid (*v.* MANDRAGORA ROOT, vol. iii. p. 391).

Meteloidine $C_{13}H_{21}O_4N$ was obtained by Pyman and Reynolds (Chem. Soc. Trans. 1908, 93, 2077) from *Datura meteloides* (DC.) along with atropine, and hyoscine (scopolamine) to the extent of 0·07 p.c. It crystallises in tabular needles, m.p. 141°–142°, and furnishes a crystalline, optically inactive hydrobromide $B{\cdot}HBr,2H_2O$, m.p. 250° (anhydrous), and an aurichloride, m.p. 149°–150°. On hydrolysis by baryta water meteloidine furnishes tiglic acid $CHMe:CMe{\cdot}COOH$ and a new base *teloidine* $C_8H_{15}O_3N$, which crystallises with $1H_2O$ and has m.p. 168°–169° (anhydrous); the aurichloride $B{\cdot}HAuCl_4,\frac{1}{2}H_2O$ has m.p. 225°, and crystallises in hexagonal plates.

Norhyoscyamine $C_{16}H_{21}O_3N$ occurs in *Scopolia japonica* (Maxim.) and *Datura Metel* (Linn.) and other solanaceous plants. On treatment with methyl iodide it yields hyoscyamine, which is its nitrogen methyl derivative. Lævorotatory: mydriatic but less so than hyoscyamine (Carr and Reynolds, Trans. Chem. Soc. 1912, 101, 946). Dilute alkalis racemise it to noratropine.

Pseudohyoscyamine $C_{17}H_{23}O_3N$ occurs, according to Merck (Arch. Pharm. 1893, 231, 117), in *Duboisia myoporoides* (R. Br.) along with hyoscyamine and scopolamine, and according to Hesse in mandragora root. It crystallises in needles, m.p. 133°–134° (decomp.), is lævorotatory $[\alpha]_D = -21{\cdot}15°$, and is hydrolysed by baryta water into tropic acid and a base $C_8H_{15}ON$ not identical with tropine or pseudotropine. According to Carr and Reynolds, pseudohyoscyamine is impure norhyoscyamine (*v. supra*).

Scopolamine (*Hyoscine*) $C_{17}H_{21}O_4N$. This alkaloid was isolated by Ladenburg (Annalen, 1880, 206, 299) from the 'amorphous hyoscyamine' remaining in the mother liquors resulting from the preparation of hyoscyamine from *Hyoscyamus niger* (Linn.), and was named by him 'hyoscine.' Some years later Schmidt obtained from *Scopolia japonica* (Maxim.) and *S. carniolica* (Jacq.) a new crystalline alkaloid, which he named scopolamine (Arch. Pharm. 1890, 228, 139, 435), and which he afterwards proved to be the principal constituent of Ladenburg's amorphous hyoscine (*ibid.* 1892, 230, 207; 1894, 232, 409; *cf.* Hesse, Annalen, 1892, 271, 120; 1893, 276, 84). Schmidt subsequently obtained scopolamine from *Hyoscyamus niger* (Linn.), *Atropa Belladonna* (Linn.), *Datura Stramonium* (Linn.), and *Duboisia myoporoides* (R. Br.). The name scopolamine has been adopted generally for this alkaloid although hyoscine is still used in commerce. A further complication in nomenclature was introduced when Hesse isolated from scopolamine hydrobromide of commerce an optically inactive alkaloid, which he named *atroscine* (Annalen, 1892, 271, 121), and which Gadamer showed subsequently was an anhydrous *i*-scopolamine (Arch. Pharm. 1898, 236, 382), Schmidt having previously shown (*ibid.* 1894, 232, 394) that when natural *l*-scopolamine hydrobromide is treated with moist silver oxide it is converted into an optically inactive isomeride (*i*-scopolamine).

Preparation. The total alkaloid is separated from the plant by the method described already. The scopolamine remains in the alcoholic solution when the atropine and hyoscyamine have crystallised out. It may be completely purified by conversion into the aurichloride, which is crystallised until it has the proper melting-point, the alkaloid being regenerated in the usual way. The usual source of the alkaloid is stated to be the mother liquors resulting from the preparation of hyoscyamine from henbane seeds or *Duboisia* roots or leaves, but it is the chief alkaloid in *Datura Metel* (Linn.), and *D. fastuosa* (Linn.) (Schmidt, Arch. Pharm. 1906, 244, 66), and certain species of *Scopolia*, and *D. Metel* especially would form a good source of the alkaloid.

Properties. Crystallises with difficulty in prisms, m.p. 59°. Soluble in alcohol or ether, slightly soluble in water. In alcoholic solution lævorotatory $[\alpha]_D = -13{\cdot}7°$, $-18°$ (Gadamer), $-28°$ in water (Gadamer); the rotation is much diminished by addition of soda (Hesse). Its mydriatic power is stated to be greater than that of atropine. The ordinary salts are crystalline. The hydrobromide $B{\cdot}HBr,3H_2O$ crystallises in rhombic tables, m.p. 187°–191° (anhydrous), $[\alpha]_D = -22{\cdot}5°$ in water (Hesse), $-15{\cdot}72°$ in alcohol (Gadamer). The aurichloride $B{\cdot}HAuCl_4$ is less soluble than the corresponding hyoscyamine compound. It crystallises well from diluted hydrochloric acid, m.p. 198° (Ladenburg, *l.c.*), and is characteristic. The picrate has m.p. 180°–181°.

Reactions. Scopolamine, for the most part, reacts like atropine and hyoscyamine, but it does not precipitate mercuric oxide from mercuric chloride. When treated with moist silver oxide *l*-scopolamine is converted into an optically inactive form, *i*-scopolamine, which crystallises with $1H_2O$ in needles or rhombohedra, m.p. 55°–56°, and yields an aurichloride $B{\cdot}HAuCl_4$, m.p. 208°–210° (Schmidt, *ibid.* 1894, 232, 394). Hesse's atroscine (Ber. 1896, 29, 1776) prepared from commercial scopolamine hydrobromide is, according to Gadamer (Arch. Pharm. 1898, 236, 382; *cf.* Schmidt, *ibid.* 9, 47), *i*-scopolamine crystallised with $2H_2O$; it has m.p. 36°–37°, and furnishes an aurichloride, m.p. 201°–202° (Hesse). When hydrolysed by acids or alkalis scopolamine yields *tropic acid* and *scopoline* (oscine) $C_8H_{13}O_2N$, which crystallises in needles, m.p. 109°, b.p. 241°–243°. Like its analogue tropine, scopoline forms esters with acids and a number of these, known as 'scopoleines,' have been prepared.

Detection. Scopolamine is readily distinguished from its associates by the higher m.p. (198°) of its aurichloride. At present the repeated recrystallisation of this salt, until it has the proper melting-point, is the only known method of purifying the alkaloid.

Baptitoxine. *See Cytisine* (p. 651).

Bebeerine $C_{18}H_{21}O_3N$ is found in bebeeru bark (*Nectandra Rodioei* (Hook.)), and true pareira root (*Chondodendron tomentosum* [Ruiz. and Pav.]), and is probably identical with buxine, contained in *Buxus sempervirens* (Linn.), and probably also with the pelosine of *Cissampelos Pareira* (Linn.). Crystallises from methyl alcohol in colourless prisms, m.p. 214, $[\alpha]_D -298°$. Forms crystalline salts. Contains one —OH and one ·OMe group. Behaves as a tertiary base. Used as a febrifuge, as a substitute for quinine. The subsidiary alkaloid *sepeerine* occurs in bebeeru bark, whilst the leaves of *Buxus sempervirens* (Linn.) also contain *parabuxine*, *buxinidine*, and *parabuxinidine*. The chief papers on the subject are Maclagan, Annalen, 1843, 48, 106; 1845, 55, 105; von Planta, *ibid.* 1851, 77, 333; Walz, J. 1860, 548; Faure, J. 11, 245; Wiggers, Annalen, 1840, 33, 81; Scholtz, Ber. 1896, 29, 2054; Arch. Pharm. 1898, 236, 530; 1906, 244, 555; 1911, 249, 408; 1913, 251, 136; and Hildebrandt, Arch. expt. Path. Pharm. 1907, 57, 279).

Belladonnine. *See* under *Atropine* (p. 637).

Berbamine. *See* under *Berberine* (*v. infra*).

Berberine and the Berberis Alkaloids.

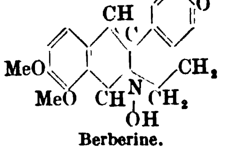
Berberine $C_{20}H_{17}O_4N,H_2O$ is contained in various species of *Berberis*, especially *B. vulgaris* (Linn.) (the barberry), which also contains berbamine $C_{18}H_{19}O_3N$ (Hesse, Ber. 1886, 19, 3193), and oxyacanthine (*v. infra*), in *Hydrastis canadensis* (Linn.), along with hydrastine (*see* p. 654), in *Coptis Teeta* (Wall.), which contains as much as 8 p.c., and in many other plants, but not in calumba root (Gordin, Arch. Pharm. 1902, 240, 146).

Preparation. The best available material from which to extract berberine is the root of *Hydrastis canadensis* (Linn.), which contains about 4 p.c. of the alkaloid. The finely-powdered hydrastis root is exhausted with alcohol, the greater part of the alcohol removed by distillation, and the alkaloid converted into sulphate or nitrate by the addition of sufficient dilute sulphuric acid or nitric acid. The crude berberine salt which separates is collected, dissolved in water, and sodium hydroxide and acetone added, whereby the alkaloid is precipitated in the form of its crystalline additive product with acetone, from which it is recovered as the hydrochloride by prolonged ebullition with chloroform and alcohol. The berberine is finally crystallised from water or alcohol.

Detection and estimation. For the detection of berberine in plants, *see* Gordin, Arch. Pharm. 1902, 240, 146. The same author recommends for estimation the precipitation of the alkaloid as sulphate from its alcohol solution, the decomposition of the sulphate by potassium iodide and the titration of the sulphuric acid liberated by means of N/40 potassium hydroxide (*ibid.* 1901, 239, 638).

Properties. Long, silky, yellow, needle-shaped crystals. Crystallised from water the substance contains $5\frac{1}{2}H_2O$; dried at 100° the crystals retain $2\frac{1}{2}H_2O$ (Perkin, Chem. Soc. Trans. 1889, 55, 63); m.p. 160° (decomp.). Slightly soluble in cold water or alcohol, but freely soluble in the hot liquids, slightly soluble in benzene or chloroform, insoluble in ether or light petroleum. Its aqueous solution is neutral to litmus, optically inactive, and has a bitter taste. The alkaloid is not poisonous to man, and is used medicinally, like preparations of the plants containing it, as a tonic. The ordinary salts of berberine crystallise well, and are of a yellow or red colour. They are sparingly soluble in water, especially in presence of mineral acids or salts.

Reactions. On adding excess of hydrochloric, sulphuric, or nitric acid, to a solution of berberine the salts separate as crystalline precipitates. Alkalis colour berberine brown. Chlorine water gives with a solution of the hydrochloride a bright-red coloration even in very dilute solutions. With alkaline permanganate berberine yields as chief products *berberal* $C_{20}H_{17}O_7N$ and *berberilic acid* $C_{20}H_{17}O_9N$. The former on hydrolysis gives noroxyhydrastinine and ψ-opianic acid. These reactions indicate that berberine has the following constitution (*cf.* Perkin, Chem. Soc. Trans. 1889, 55, 63; 1890, 57, 1081; 1910, 97, 305; Tinkler, *ibid.* 1911, 99, 340; Gadamer, Chem. Zeit. 1902, 26. 291, 385; Arch. Pharm. 1905, 243, 31; 1910, 248, 43). A synthesis of berberine has been effected by Pictet and Garus (Compt. rend. 1911, 152, 1102; 153, 386):—



Berberine.

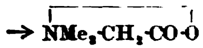
Berberine is therefore closely allied to hydrastine, which occurs with it in *Hydrastis canadensis* (Linn.), and also to the two opium alkaloids, papaverine and narcotine.

Oxyacanthine $C_{19}H_{21}O_3N$ accompanies berberine in *Berberis vulgaris* (Linn.) (Polex, Arch. Pharm. 1836, 45, 271; Hesse, Ber. 1886, 19, 3190; Rüdel, *ibid.* 1891, 229, 631), and may be obtained by precipitating with soda the mother-liquor from which all the berberine salt has crystallised (Hesse). It crystallises with difficulty from alcohol or ether, m.p. 208°–214° (Hesse), is insoluble in water, easily soluble in chloroform, less so in alcohol. The alcoholic solution is dextrorotatory, alkaline to litmus, and has a bitter taste. The ordinary salts crystallise.

Betäine $C_5H_{11}O_2N$ (*lycine, oxyneurine*) (*v.* also vol. i. p. 452) occurs in sugar-beet and in numerous other plants. Crystalline, m.p. 293° (dry), optically inactive. Sweet taste. The hydrochloride has been used in medicine. It is formed by the oxidation of choline (p. 645), and by the action of trimethylamine on chloroacetic acid

$$CH_2Cl\cdot COOH + NMe_3 \rightarrow Cl\cdot NMe_3\cdot CH_2\cdot COOH$$

Chloroacetic acid. Trimethylamine. Betäine hydrochloride.



$$\rightarrow NMe_3\cdot CH_2\cdot CO\cdot O$$

Betäine.

The special anhydride grouping (betāine grouping) characteristic of betāine occurs in several natural alkaloids, *e.g.* chrysanthemine (p. 645), strychnine (p. 676), and trigonelline (p. 680).

Brucine. *See* under *Strychnine* (p. 678).

Bulbocapnine. *See* under *Corydaline* (p. 650).

Buxine, Buxinidine, Parabuxine, &c. *See Bebeerine* (p. 639).

Caffearine $C_{14}H_{16}O_4N_2$, an alkaloid occurring with caffeine (*see* below) in coffee berries. Hygroscopic needles, m.p. 140° (decomp.). Optically inactive. Weakly alkaline (Palladino, Chem. Soc. Abstr. 1894, 66, [i.] 214; 1895, 68, [i.] 629). According to Gorter (Annalen, 1910, 372, 237) caffearine is identical with trigonelline.

Caffeine and the Alkaloids of Tea, Coffee and Cocoa.

These bases are nearly related to uric acid, a substance only found in the animal organism.

Caffeine (*Theine*) $C_8H_{10}O_2N_4$, the principal alkaloid of tea and coffee, is also found in guarana, maté or Paraguay tea, kola nuts, and in small amounts in cocoa (Schmidt, Annalen, 1883, 217, 306). Coffee beans are stated to contain an average of about 1 p.c. of caffeine, and tea leaves 1–4·8 p.c. (Stenhouse, *ibid.* 1853, 89, 244; 102, 124; Chem. Soc. Mem. 1, 215; Chem. Soc. Trans. 1856, 9, 33; *cf.* Bull. Imp. Inst. 1908, 6, 1). More recent determinations conducted with improved methods have shown that ordinary samples of tea leaves contain from 3–4 p.c. of caffeine, whilst commercial samples of coffee show a remarkable uniformity in containing less than 1·5 p.c. of the alkaloid (Paul and Cownley, Pharm. J. 1886–1887, [iii.] 17, 565, 821, 921; 1890–1891, [iii.] 21, 61; Dvorkovitch, Ber. 1891, 24, 1945; *cf.* Bull. Imp. Inst. 1908, 6, 1, and Coffee. Vol. II. p. 97).

According to Kossel (Zeitsch. physiol. Chem. 1889, 13, 298) tea also contains small quantities of *theophylline* (*see* p. 642), *hypoxanthine*, or *sarcine* ($C_5H_4ON_4$), *iminosarcine* or *adenine* ($C_5H_5N_5$), and *xanthine* ($C_5H_4O_2N_4$), of which caffeine is the trimethyl derivative.

Preparation. Tea is heated for about an hour with four times its weight of boiling water, the solution is filtered and mixed with a weight of lime equal to that of the tea taken, and the mixture dried on the water-bath. The powdered residue is exhausted with boiling chloroform, which dissolves the caffeine. The alkaloid is purified by crystallisation from alcohol or water (Cazeneuve and Caillol, Bull. Soc. chim. 1877, [ii.] 27, 199; *cf.* Paul, Pharm. J. 1890–1891, [iii.] 21, 882). Or the methods described for the extraction of theobromine (*see* below) may be employed. Caffeine may be extracted from coffee and the other substances which contain it by similar methods.

Properties. Silky needles, containing $1H_2O$ from water, anhydrous from alcohol, chloroform, or benzene. The hydrate loses its water at 100°, and the anhydrous caffeine melts at 234°–235° (Strecker, Annalen, 1861, 118, 170; Dunstan and Shepheard, Chem. Soc. Trans. 1893, 63, 197). Sublimes without decomposition. Soluble in cold water (1 in 80 at 15°), readily soluble in boiling water. Sparingly soluble in ether or absolute alcohol, more soluble in aqueous alcohol. Very soluble in chloroform (13 in 100 at 16°). The aqueous solution is neutral and has a bitter taste.

Caffeine is a very weak, monacidic base. It dissolves in aqueous acids forming salts which crystallise, but are decomposed on evaporation of their aqueous solutions, which, indeed, would seem to contain free alkaloid under ordinary conditions, since caffeine can be extracted from them by shaking with chloroform. The salts of caffeine with organic acids are particularly unstable. The double salts are more stable. The aurichloride $B{\cdot}HAuCl_4$ and mercuric chloride compound $B{\cdot}HgCl_2$ crystallise well (Nicholson, Annalen, 62, 71; Schmidt, *ibid.* 1883, 217, 283; Ber. 1881, 14, 814). The aurichloride melts at 242·5°, and is soluble in alcohol, and to a smaller extent in water. It is decomposed when its aqueous solution is warmed, with loss of two molecular proportions of hydrochloric acid, forming aurichlorcaffeine $C_8H_9(AuCl_2)O_2N_4$, m.p. 207°, insoluble in water or alcohol: this dissolves in aqueous hydrochloric acid, reproducing the aurichloride (D. and S.). Caffeine does not unite directly with auric chloride, but it combines with potassium auric chloride, forming a red crystalline compound $B{\cdot}KAuCl_4$, m.p. 208°. This is precipitated by mixing a solution of caffeine in chloroform with an alcoholic solution of potassium auric chloride, and is resolved into its constituents on solution in water or acetone (D. and S. *l.c.* 205). The 'citrate' $B{\cdot}C_6H_8O_7$ is a colourless powder, soluble in water (1 in 3; more water dissociates the salt forming caffeine which re-dissolves in excess of water, 1 in 32). This salt, as well as caffeine itself, is used in medicine.

For information concerning other caffeine salts, the papers of Nicholson and Schmidt, referred to above, should be consulted.

Reactions. Caffeine is precipitated by several of the alkaloidal reagents, notably tannic acid and iodine solution in presence of acid, but not by Mayer's solution. It exhibits the murexide reaction (p. 642), the oxidation being best effected by evaporating a solution of caffeine in hydrochloric acid with a crystal of potassium chlorate.

Caffeine is methyltheobromine and consequently trimethylxanthine (Fischer, Ber. 1898, 31, 2563). It may be prepared by heating silver theobromine with methyl iodide (Strecker, Annalen, 1861, 118, 170). The constitution of caffeine and its relationship to other alkaloids of this group is discussed below.

Estimation of caffeine in tea and coffee. A number of methods have been proposed for this purpose. Allen's modification of Stahlschmidt's process gives good results: 6 grms. of the finely-powdered tea are boiled under a reflux apparatus during 6–8 hours with 500 c.c. of water. The filtered extract is diluted to 600 c.c., heated almost to boiling, 4 grms. of lead acetate added, and the boiling continued for 10 mins. 500 c.c. of the filtrate are evaporated to 50 c.c., and the excess of lead removed by adding sodium phosphate. The filtrate is concentrated to 40 c.c., and the caffeine extracted by shaking at least 4 times with chloroform. The total chloroformic solution is run into a tared flask, the solvent distilled off and the residue dried by a current of warm, dry, filtered air and weighed. Its weight multiplied by 20 gives the percentage of caffeine in the tea. (For other processes, *see* Paul and Cownley, Pharm. J. 1887–1888, [iii.] 18, 417; Vité, Chem. Zentr. 1890, ii. 274; Dvorkovitch, Ber. 1891, 24, 1945.) These methods also answer for coffee if a larger quantity of the material is taken.

Theobromine $C_7H_8O_2N_4$ occurs in cocoa beans (*Theobroma Cacao* [Linn.]), and is also stated to be present in minute amounts in tea leaves and kola nuts (*cf.* Dekker, Rec. trav. chim. 1903, 22, 143). Cocoa beans usually contain 1–2 p.c. of theobromine; the nibs or shells of the beans contain about 0·5 p.c. *V.* also Cocoa, vol. ii. p. 91.

Preparation. Finely-powdered cocoa beans are exhausted with boiling water. Lead acetate solution is then added until no further precipitate is obtained. By this means tannin, organic acids, and colouring matter are removed. The filtrate is freed from lead by hydrogen sulphide, and evaporated to dryness. The residue is boiled with alcohol to dissolve the theobromine, which crystallises when the alcoholic solution is evaporated. Or the powdered beans may be mixed with about half their weight of quicklime, and the mixture boiled with alcohol (80 p.c.), which dissolves the theobromine (Schmidt and Pressler, Annalen, 1883, 217, 288; Dragendorff, Ber. 1878, 11, 1689).

Estimation. The method described by Dekker (Rec. trav. chim. 1903, 22, 143) is stated to give good results.

Properties. Microscopic needles which sublime when heated at 290°–295°, m.p. 329° (under pressure) (Keller, Annalen, 1854, 92, 71, 329; Michael, Ber. 1895, 28, 1629). Slightly soluble in water (1 in 1600 at 17°; 1 in 148·5 at 100°) or ether, rather more soluble in chloroform (1 in 105 at 62°). Very slightly soluble in absolute alcohol, more soluble in aqueous alcohol (rectified spirit, 1 in 47 at b.p.). Theobromine possesses both acid and feebly basic properties. It dissolves in aqueous alkalis, and the solution yields metallic derivatives, which crystallise with difficulty and are decomposed by carbon dioxide, theobromine being liberated. The silver compound

$AgC_7H_7O_2N_4,1\frac{1}{2}H_2O$

is insoluble in water. It is produced as a semi-crystalline precipitate when silver nitrate is added to a solution of theobromine in aqueous ammonia (Schmidt, Annalen, 1883, 217, 282).

Theobromine acts as a monacidic base. It unites with acids, forming crystalline salts, which, as a rule, are decomposed by boiling with water (Schmidt and Pressler, *ibid.* 1883, 217, 289).

Reactions. Theobromine is precipitated by several of the alkaloid reagents, but not by Mayer's solution. It is most easily detected by a reaction which is very similar to the murexide reaction for uric acid. The theobromine is first oxidised by warming it with chlorine water, or a drop of nitric acid, and evaporating to dryness. The residue consists chiefly of amalic acid (tetramethylalloxantin $C_8(CH_3)_4O_7N_4$). The residue is coloured violet by potash and bright red by ammonia, owing to the formation of tetramethylmurexide. This reaction is very delicate, but it is also exhibited by the other alkaloids of this group.

The constitution of theobromine and its relation to other alkaloids of this group is discussed below.

Theobromine is dimethylxanthine and may be prepared from xanthine (*see* below) by heating its lead or silver derivative with methyl iodide at 100° (Fischer, Annalen, 1882, 215, 311).

Theophylline $C_7H_8O_2N_4$, an isomeride of theobromine, which occurs in small quantity in tea leaves (Kossel, Zeitsch. physiol. Chem. 1888, 13, 298; Ber. 1888, 21, 2164).

Preparation. A large quantity of tea is exhausted by extraction with alcohol, and the solution evaporated to a syrup, from which the greater part of the caffeine will crystallise out. This is removed, and the liquid residue diluted with water acidified with sulphuric acid. After having stood for some hours the liquid is filtered, the filtrate made alkaline with ammonia, and precipitated by solution of silver nitrate. After the lapse of 24 hours the precipitate is filtered off, washed, and dissolved in a little warm nitric acid (sp.gr. 1·1). On cooling the silver derivatives of sarcine and adenine crystallise out, leaving the silver theophylline dissolved. The acid filtrate is made alkaline with ammonia, and the precipitate of silver theophylline, &c. collected, washed, suspended in water acidified with nitric acid, and decomposed by hydrogen sulphide. By evaporating the filtrate crystals of xanthine separate, and afterwards the theophylline crystallises. A further quantity may be obtained from the mother liquor by precipitation with mercuric nitrate and decomposition of the precipitate with hydrogen sulphide (Kossel, *l.c.*).

Properties. Tabular crystals, with $1H_2O$, m.p. 264°. Readily soluble in boiling water. Slightly soluble in cold alcohol. Like theobromine, it affords the 'murexide' reaction, and in general its decomposition products are similar. When silver theophylline is heated with methyl iodide caffeine is formed.

Constitution of caffeine and the related alkaloids. Alkaloids of this type are somewhat widely distributed in plants and animals. Thos occurring in plants are as follows:—

Adenine $C_5H_5N_5$ in tea and beetroot.

Guanine $C_5H_5ON_5$ in many leguminos plants, and as its pentoside *vernine* $C_{10}H_{13}O_5N_5$ in the seeds of *Vicia sativa* (Linn.), &c. (Schulz and Castoro, Zeitsch. physiol. Chem. 1904, 41, 463); also in guano.

Hypoxanthine $C_5H_4ON_4$ in black pepper, and as its pentoside *inosine* $C_{10}H_{12}O_5N_4$ in yeas and beetroot, and in meat extract (Haiser an Wenzel, Monatsh. 1908, 29, 157).

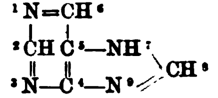
Xanthine $C_5H_4O_2N_4$ in tea.

Theophylline $C_7H_8O_2N_4$ in tea.

Theobromine $C_7H_8O_2N_4$ in cocoa.

Caffeine $C_8H_{10}O_2N_4$ in tea, coffee, kola.

Certain of these also occur in animals and uri acid, $C_5H_4O_3N_4$ is found in animals only. All these compounds may be regarded as derived from a parent substance purine (Fischer, Ber. 1899, 32, 435), which has so far not been found occurring naturally.



Purine.

The substances of practical importance are caffeine, theobromine, and theophylline, to which may be added uric acid, since it occurs in guano and is prepared from that source to be used as a raw material in the industrial manufacture of the three alkaloids just named. The constitution of uric acid is established by its synthesis accomplished by the following series of reactions (Fischer and Ach, Ber. 1895, 28, 2473):—

(1) Condensation of malonic acid with carbamide (urea) to form malonylcarbamide.

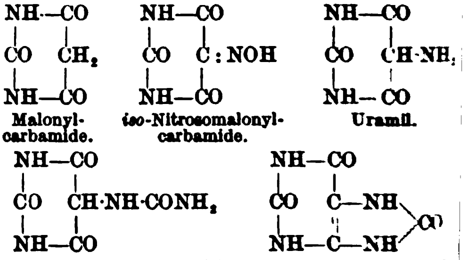
(2) Conversion of malonylcarbamide into its *iso*nitroso- derivative (violuric acid) by the action of nitrous acid.

(3) Reduction of *iso*nitrosomalonylcarbamide to the corresponding amino derivative (uramil).

(4) Conversion of uramil into *pseudo*uric acid by the action of potassium cyanate.

(5) Transformation of *pseudo*uric acid into uric acid by the action of hot dilute acid.

This series of changes may be represented thus—



Malonyl-carbamide. *iso*-Nitrosomalonyl-carbamide. Uramil.

pseudo-Uric acid. Uric acid (2:6:8-Trioxypurine).

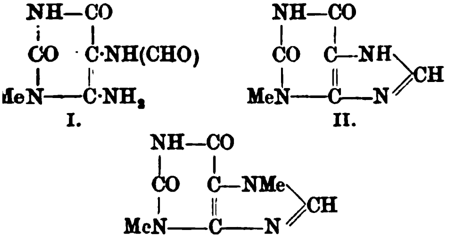
Adenine $C_5H_5N_5,3H_2O$, long needles, m.p. 360°–365°, is 6-aminopurine (p. 47, vol. i.).

Guanine $C_5H_5ON_5$, colourless amorphous powder, is 2-amino-6-oxypurine (p. 12, vol. iii.)

Hypoxanthine $C_5H_4ON_4$, microscopic needles, decomposes at 150°, is 6-oxypurine (p. 91, vol. iii.).

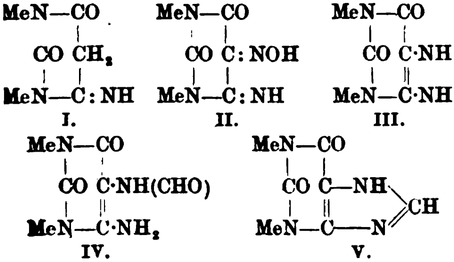
Xanthine $C_5H_4O_2N_4$, colourless powder, is 2:6-dioxypurine (p. 791, vol. v.).

Theobromine $C_7H_8O_2N_4$ (for description, *see* bove). The synthesis of this alkaloid has been ccomplished by a series of reactions analogous o that described for theophylline (*v. infra*). 'or this purpose methylcarbamide is used as a tarting-point, leading eventually to the formyl lerivative of 4 : 5-diamino-2 : 6-dioxypyrimidine I) ; this, on loss of water, forms 3-methyl-anthine (II) ; which, on methylation, gives heobromine (3 : 7-dimethylxanthine or 3 : 7-limethyl-2 : 6-dioxypurine) (III)—


I. II.

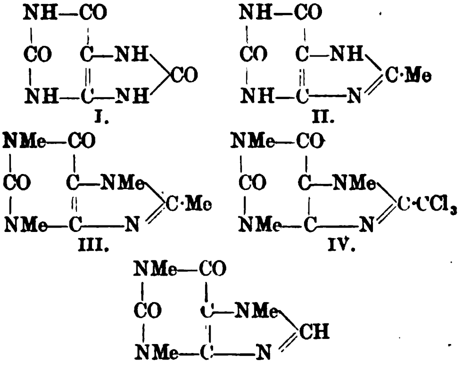
III. (Theobromine).

Theophylline $C_7H_8O_2N_4$ (for description, *see* above). This alkaloid has been synthesised by a series of reactions similar to those described for uric acid, and it may also be prepared from the latter. It is prepared commercially from uric acid or from dimethylcarbamide (Traube, Ber. 1900, 33, 3035). Dimethylcarbamide is condensed with cyanoacetic acid in presence of phosphorus oxychloride forming dimethylimino-barbituric acid (I), which by the action of nitrous acid is converted into the oximino compound (II). The latter on reduction forms 1 : 3-dimethyl-4 : 5-diamino-2 : 6-dioxypyrimidine (III), which with formic acid yields a formyl-derivative (IV); this on heating loses 1 mol. of water forming theophylline (V) (1 : 3-dimethyl-2 : 6-dioxypurine or 1 : 3-dimethylxanthine).


I. II. III.

IV. V.

Caffeine $C_8H_{10}O_2N_4$ (for description, *see* above). This alkaloid results from the methylation of xanthine, theophylline, or theobromine, so that the synthetic processes already described for the two latter alkaloids are also suitable for caffeine, provided the product obtained is methylated. Caffeine is therefore 1 : 3 : 7-trimethylxanthine (1 : 3 : 7-trimethyl-2 : 6-dioxypurine). Synthetic caffeine is manufactured chiefly from uric acid (I) by heating this with acetic anhydride (Böhringer and Söhne, D. R. P. 121224), when it is converted into 8-methylxanthine (II), which is then methylated completely, forming 1 : 3 : 7 : 8-tetramethylxanthine (III). The latter is fully chlorinated in the 8th position, and the resulting 1 : 3 : 7-trimethyl-8-trichloroxanthine (IV) treated with potash when caffeine (V) results.


I. II.

III. IV.

V. (Caffeine).

Calabarine. *See* under Physostigmine.

Calycanthine $C_{11}H_{14}N_2$, crystals, m.p. 243°–244° (dry), occurs with *iso*calycanthine, prisms, m.p. 235°–236° (dry), in the seeds of *Calycanthus glaucus* (Wild.). One nitrogen is secondary, the other tertiary. Toxic (Gordin, J. Amer. Chem. Soc. 1905, 27, 144, 1418 ; 1909, 31, 1305 ; 1911, 33, 1626).

Canadine. *See* under *Hydrastine* (p. 655).

Carpaine $C_{14}H_{25}O_2N$ occurs in papaw leaves (*Carica Papaya* (Linn.)). It forms glancing prisms, m.p. 121°, $[\alpha]_D + 21° 55'$, and has a bitter taste. A heart poison (Greshoff, 1890, Med. s'Lands Plantentuin, Java, No. 7, 5 ; van Rijn, Arch. Pharm. 1893, 231, 184 ; 1897, 235, 332). According to Barger (Chem. Soc. Trans. 1910, 97, 466) it is a lactone of carpamic acid $C_{14}H_{27}O_3N$.

Casimiroine $C_{24}H_{20}O_8N_2$, rosettes of colourless needles, m.p. 196°–197°, occurs in the seeds of *Casimiroa edulis* (LaLlave); the picrate, m.p. 165°, and aurichloride, m.p. 195°–196°, are crystalline. Contains two methoxyl groups, and on hydrolysis by alkalis yields *casimiroitine* $C_{23}H_{22}O_7N_2$, m.p. 171°, apparently by loss of CO_2 and absorption of H_2O. The seeds also contain *casimiroedine* $C_{17}H_{24}O_5N_2$, aggregates of small needles, m.p. 222°–223°, $[\alpha]_D - 36{\cdot}5°$ (in acid solution). Casimiroine and casimiroedine are physiologically inactive (Power and Callan, Chem. Soc. Trans. 1911, 99, 1993 ; *cf.* Bickern, Arch. Pharm. 1903, 241, 166 ; and Vincent, Bl. Gen. Ther. 1909, 158, 16, 96, 193, 241).

Cephaeline. *See* under *Emetine* (p. 652).

CEVADINE AND THE ALKALOIDS OF VERATRUM SPP.

The species principally concerned are the seeds of *Schoenocaulon officinale* (A. Gray) [*Asagræa officinalis* (Lindley)], and the rhizomes of *Veratrum viride* (Ait.) (green hellebore) and *Veratrum album* (Linn.) (white hellebore), all of which belong to the N. O. *Liliaceæ*, and have nothing in common with the hellebores proper, which belong to the N. O. *Ranunculaceæ*. The alkaloids present in these three drugs are as follows :—

Sabadilla seeds	Cevadine (crystallised veratrine) Veratridine (amorphous veratrine) Sabadilline (cevadilline) Sabadine Sabadinine

White Hellebore	Protoveratrine Jervine Pseudojervine Rubijervine Protoveratridine Veratralbine
Green Hellebore	Cevadine Veratridine Jervine Pseudojervine Veratralbine

It should be noted that there has been considerable confusion in the nomenclature of these alkaloids. Commercially the name 'veratrine' is applied to an amorphous mixture of alkaloids obtained from sabadilla seeds. The name veratrine is also frequently applied to veratridine, usually, however, with the prefix 'amorphous.' The name veratridine was also applied by Robbins (Pharm. J. 1877–1878, [iii.] 8, 316) to a crystalline alkaloid contained in green hellebore, and which, in some respects, resembles protoveratrine. It is not identical with Bossetti's veratridine isolated from sabadilla seed (Ber. 1883, 16, 1384).

Alkaloids of Sabadilla Seeds.

Cevadine (*crystallised veratrine*) $C_{32}H_{49}O_9N$ is the chief alkaloid of sabadilla or cevadilla seeds (*Schoenocaulon officinale* [A. Gray]).

Preparation. The finely-powdered seeds are extracted with alcohol, containing 1 p.c. of tartaric acid. The acid liquid is evaporated and diluted with water to precipitate resin. To the clear solution soda is added in slight excess, and the mixture completely extracted by repeatedly shaking with ether. The ethereal solution is mixed with light petroleum and the filtrate allowed to evaporate spontaneously. Crystals of cevadine separate from the syrup, and are recrystallised from their solution in alcohol. The remaining syrup contains veratridine (amorphous veratrine) and sabadilline (Wright and Luff, Chem. Soc. Trans. 1878, 33, 338).

Sabadilla seeds contain about 0·1 p.c. of cevadine.

'Commercial veratrine' is amorphous and appears to be a mixture of cevadine with amorphous alkaloids.

Properties. Rhombic prisms, containing $2C_2H_5OH$ when crystallised from alcohol. The alcohol is lost at 130°–140°, and the anhydrous alkaloid then melts at 205° with decomposition. Nearly insoluble in water, soluble in alcohol or ether. Optically inactive. Acts as a monacidic base, forming salts, some of which are crystalline (Merck, Annalen, 1855, 95, 200; Schmidt, Annalen, 1877, 185, 224).

The aurichloride, m.p. 182° (decomp.), and the mercurichloride, m.p. 172° (decomp.), are characteristic crystalline compounds (Ahrens, Ber. 1890, 23, 2700).

Cevadine and its salts are intensely poisonous.

Reactions. When warmed with concentrated hydrochloric acid cevadine produces a fine purplish-red colour, which is a somewhat delicate test for the alkaloid. Concentrated sulphuric acid produces a carmine-red coloration, or, if the alkaloid is previously mixed with a little sugar, a blue.

Cevadine is a monacidic tertiary base. The alkaloid unites with bromine to form a dibromide and a tetrabromide. It contains no methoxyl groups and no :NMe group; one HO· group is present.

When allowed to stand with aqueous alkalis or when heated with alcoholic potash, cevadine undergoes hydrolysis furnishing *cevine*

$$C_{27}H_{42}O_8N$$

and angelic and tiglic acids $C_5H_8O_2$ (Wright and Luff, Chem. Soc. Trans. 1878, 33, 338; 18 35, 405; Bosetti, Arch. Pharm. 1883, [iii.] 2 81; Ahrens, Ber. 1890, 23, 2700; Freund and collaborators, *ibid.* 1899, 32, 801; 1904, 3 1964). Cevine crystallises with $3\frac{1}{2}H_2O$ from dilute alcohol, m.p. 195°–200° (anhydrous), and yields derivatives both with metals and acids. It is less toxic than cevadine (Freund, *l.c.*).

When oxidised by permanganate cevadine yields acetic and oxalic acids, or when chromic acid is used, principally acetaldehyde and carbon dioxide.

When anhydrous cevadine is distilled β-picoline is obtained with tiglic acid.

Veratridine (*amorphous veratrine*) $C_{37}H_{53}O_{11}N$ is found in sabadilla seeds, and is isolated from the amorphous alkaloids precipitated in the earlier stages of the preparation of cevadine (*see* above) by treating this with ether when it separates into insoluble matter (sabadilline) and soluble matter (veratridine). The latter is purified by conversion into the sparingly soluble crystalline nitrate. Veratridine is said to be sternutatory. On hydrolysis by alkalis it yields *verine* $C_{28}H_{45}O_8N$, which closely resembles cevine (*see* above) and veratric acid (3 : 4 dimethoxylbenzoic acid).

Sabadilline (*cevadilline*) $C_{34}H_{53}O_8N$ is a second amorphous alkaloid occurring in sabadilla seeds. It yields amorphous salts (W. and L. *l.c.*).

Sabadine $C_{29}H_{51}O_8N$, crystals, m.p. 238°–240°, also occurs in sabadilla seeds; the salts are crystalline (Merck, Arch. Pharm. 1891, 229, 164).

Sabadinine $C_{27}H_{45}O_8N$ (?), crystals; found in sabadilla seeds; yields a crystalline aurichloride and sulphate (M. *l.c.*).

Sabadilline, sabadine, and sabadinine all resemble cevadine in action, but are less toxic.

Alkaloids of White Hellebore Rhizome.

Protoveratrine $C_{32}H_{51}O_{11}N$ is the characteristically toxic alkaloid of white hellebore 'roots.' It crystallises in thin four-sided tablets from alcohol, m.p. 245°–250°, 239°–241° (Bredemann) and dissolves in sulphuric acid with a green coloration, which gradually passes into deep blue. It is readily decomposed by acids yielding *iso*butyric acid as one product.

Protoveratrine is accompanied in white hellebore rhizomes by

Jervine $C_{26}H_{37}O_3N$, prismatic crystals, m.p. 238°–242°; toxic.

Pseudo*jervine* $C_{29}H_{42}O_7N$, six-sided tablets, m.p. 300°–307°; not poisonous.

Rubijervine $C_{26}H_{43}O_2N$, long prisms, m.p. 240°–246°, 234° (Bredemann); not poisonous.

Protoveratridine $C_{24}H_{45}O_8N$, four-sided plates, m.p. 265°; not poisonous.

The chief papers relating to protoveratrine and its congeners are Wright and Luff (Chem. Soc. Trans. 1879, 35, 405), Salzberger (Inaug.

Diss. Erlangen, 1890; Arch. Pharm. 1890, 228, 162), Pehkschen (Inaug. Diss. Dorpat, 1890; J. Pharm. Chim. 1890, [v.] 22, 265), and Bredemann (Apoth. Zeit. 1906, 21, 41, 53).

Alkaloids of Green Hellebore Rhizome.

The chief alkaloids occurring in this drug have been described already, viz. cevadine (*see* under *Alkaloids of sabadilla seeds*), jervine, and pseudojervine (*see* under *Alkaloids of white hellebore rhizome*). Veratridine (*see* under *Alkaloids of sabadilla seeds*) occurs only in traces in green hellebore. Robbins isolated from green hellebore rhizomes (Pharm. J. 1877–1878, [iii.] 8, 316) a crystalline alkaloid which he called veratridine, and which, like protoveratrine of white hellebore, gives a green coloration with sulphuric acid. The amorphous alkaloid veratralbine was also obtained by Wright and Luff from this source (Chem. Soc. Trans. 1879, 35, 421).

Cheirinine. *See* under *Cheiroline.*

Cheiroline $C_5H_9O_2NS_2$, colourless prisms, m.p. 47°–48°, optically inactive, occurs in wallflower seeds (*Cheiranthus Cheiri* [Linn.]) and *Erysimum nanum* (Boiss. & Hohen.). On hydrolysis by dilute alkalis it yields carbon dioxide, hydrogen sulphide, and a substance $C_4H_{11}O_2NS$. It is stated to possess antipyretic properties (Wagner, Chem. Zeit. 1908, 32, 76; Schneider, Ber. 1908, 41, 4466; 1909, 42, 3416). From wallflower leaves or seeds Reeb has obtained *cheirinine* $C_{18}H_{35}O_{17}N_3$, which resembles quinine in physiological action (Arch. expt. Path. Pharm. 1898. 41, 302; 1899, 43, 130) and a glucoside cheiranthin.

Chelerythrine $C_{21}H_{17}O_4N$ occurs in various Papaveraceous plants, *e.g. Chelidonium majus* (Linn.), *Glaucium flavum* (Crantz.), *Sanguinaria canadensis* (Linn.) (Probst, Annalen, 1839, 29, 120, 250), *Bocconia* spp. Forms colourless rhombohedra with $1H_2O$ or $1C_2H_5OH$, m.p. 203°, $[\alpha]_D=0°$. Salts intensely yellow and well crystallised. Contains two methoxyl groups, and may be a methyl ether of sanguinarine (p. 675). Narcotic (König and Tietz, Arch. Pharm. 1893, 231, 145, 161; Murrill and Schlotterbeck, Ber. 1900, 33, 2802; Fischer, Arch. Pharm. 1901, 239, 409, 426, 438).

Chelidonine $C_{20}H_{19}O_5N,H_2O$ occurs with protopine, chelerythrine, sanguinarine, and α-, β-, and γ-homochelidonines in the root of the common celandine (*Chelidonium majus* [Linn.]), and with one or more of the same alkaloids in *Stylophorum diphyllum* (Nutt.) (Selle, Arch. Pharm. 1890, 228, 96), *Adlumia cirrhosa* (Rafin.) (*see* under *Adlumine*), and possibly in *Sanguinaria canadensis* (Linn.) (König and Tietz, Arch. Pharm. 1893, 231, 145, 161). It crystallises in monoclinic tablets, m.p. 135°–136°, $[\alpha]_D+115°24'$. Yields a benzoyl derivative, m.p. 217°, and when heated with zinc-dust furnishes ammonia and a substance with a phenanthrene-like odour (Schlotterbeck and Watkins, Pharm. Arch. 1903, 6, 141). Salts crystallise well (Wintgen, *ibid.* 1901, 239, 438). It is slightly toxic, resembling morphine in its action.

Chloroxylonine $C_{22}H_{23}O_7N$, an alkaloid occurring in East Indian satinwood (*Chloroxylon Swietenia* (DC.)). It crystallises from alcohol in colourless prisms, m.p. 182°–183°, $[\alpha]_D^{18}-9°18'$, in chloroform, is soluble in excess of ammonia solution, and is neutral to litmus. The salts are crystalline and dissociate in water; aurichloride $B\cdot HCl\cdot AuCl_3$ groups of reddish-yellow needles, m.p. 70°. Chloroxylonine contains four ·OMe but no hydroxyl groups (Auld, Chem. Soc. Trans. 1909, 95, 964). It produces dermatitis when applied to the skin and is the cause of the dermatitis sometimes experienced by satinwood workers (Cash, Brit. Med. J. 1911, Oct. 7; and Bull. Imp. Inst. 1911, 9, 351).

Choline $C_5H_{15}O_2N$ is an amine found in many plants, *e.g.* oats, lupins, barley, hops, potatoes, beetroot, scopolia, ipecacuanha, &c., and has long been known as a decomposition product of a number of substances occurring in the animal organism (lecithin, bile-acids, &c.). It reacts with acids like ammonium hydroxide, the acid radicle taking the place of hydroxyl. Choline is hydroxyethyltrimethylammonium hydroxide $N(C_2H_4OH)(CH_3)_3OH$; its chloride may be produced by the action of trimethylamine on ethylene chlorohydrin; *v.* also vol. ii. p. 48.

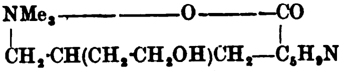
Chrysanthemine $C_{14}H_{28}O_3N_2$, crystals, occurs in *Chrysanthemum cinerariaefolium* (Vis.) flowers used under the name 'Dalmatian insect powder.' Forms crystalline salts; aurichloride

$$B\cdot 2HCl\cdot AuCl_3,$$

golden-yellow prisms. On oxidation with sodium hypobromite it forms oxychrysanthemine

$$C_{14}H_{26}O_4N_2,$$

which is a carboxylic acid. The potassium salt of this when heated with caustic potash solution gives trimethylamine, piperidinecarboxylic acid, and succinic acid, whence the following formula has been assigned to the alkaloid :—



$$\begin{array}{lcr} NMe_3 \text{———————} & O & \text{———————}CO \\ | & & | \\ CH_2\cdot CH(CH_2\cdot CH_2OH)CH_2 & \text{—} & C_5H_9N \end{array}$$

Chrysanthemine.

The alkaloid is relatively inactive physiologically (Marino-Zuco, Chem. Soc. Abstr. 1891, 60, 333; 1892, 62, 84).

Cinchonidine and **Cinchonine.** *See* under *Quinine* (p. 665).

Clavine. *See* under *Ergotoxine* (p. 652).

COCAINE AND THE COCA ALKALOIDS.

The coca leaves of commerce are derived from three varieties of the coca plant, *Erythroxylon Coca* (Lam.), viz. *E. Coca*, var. *Bolivianum* (Burck.) *E. bolivianum* (Rusby), cultivated in Bolivia; *E. Coca* var. *Truxillense* (Rusby), cultivated in Peru; and *E. Coca*, var. *spruceanum* (Burck.), cultivated in Java. *E. Coca*, var. *Novo-granatense* (Morris), and *E. Coca*, var. *Bolivianum*, are also cultivated in Ceylon and the Federated Malay States. Bolivian leaves rarely appear in European markets. The Peruvian leaves are known as Truxillo leaves. The Ceylon leaves may be either Truxillo (probably from *E. Coca*, var. *Novo-granatense*) or Bolivian (Huanuco) in character, and the Java leaves are distinct from any of these types in appearance, and in the fact that they contain little or no cocaine (*cf.* Holmes, Pharm. J. 1901, [iv.] January 5th and 26th, and Bull. Imp. Inst. 1912, 10, 37). Coca leaves contain alkaloids of four types—

1. *Cocaines;* alkyl acyl derivatives of ecgonine.

2. *Acylecgonines;* acyl derivatives of ecgonine.

3. *Pseudotropeines;* acyl derivatives of pseudotropine.

4. *Hygrines.*

The first and second types of alkaloid can be employed as commercial sources of ecgonine, and consequently can be used for the manufacture of crystalline cocaine which is readily prepared from ecgonine. The coca leaves derived from South America contain up to 1 p.c. of total alkaloids soluble in ether (mostly cocaine), the Ceylon and Federated Malay States leaves contain up to 1·6 p.c. of total alkaloid soluble in ether, of which two-thirds may be cocaine, whilst Java leaves contain 1·6, or sometimes more total alkaloids, little or none of which is cocaine, but from which a large proportion of cocaine can be prepared.

Estimation of total alkaloids in coca leaves. The following process is given in the United States Pharmacopeia, 8th ed.: 10 grms. of coca leaves in No. 60 powder are mixed with 50 c.c. of a mixture of chloroform 1 vol., ether 4 vols., in a stoppered Erlenmeyer flask and set aside during 10 mins. Two c.c. of ammonia solution diluted with 3 c.c. of water are then added and the flask shaken at intervals during 1 hour. A small glass percolator with the lower end obstructed by a wad of cotton wool is then placed in the neck of a separating funnel containing 6 c.c. of N-sulphuric acid, diluted with 20 c.c. of water and the contents of the flask poured into the percolator. When all the liquid has passed the contents of the percolator are packed in firmly by means of a glass rod, and then the flask is rinsed out with 10 c.c. of the chloroform-ether mixture, followed by several successive washings with 5 c.c. quantities of the same mixture, the percolation being continued with this liquid until 50 c.c. have been used in all. The separator is now shaken during one minute, the acid liquid drawn off, and the extraction repeated twice, using each time 10 c.c. of acid (6 c.c. N-acid with 20 c.c. of water); the combined acid liquors are made distinctly alkaline with ammonia solution and the alkaloids extracted with successive portions of ether (25, 20, and 15 c.c.). The ether is allowed to evaporate spontaneously and the residue dissolved in 4 c.c. of N/10 sulphuric acid, and the excess of acid determined by N/50 potassium hydroxide, using cochineal or iodeosin as indicator. This process gives the amount of ether-soluble alkaloids in the drug. No satisfactory process is yet available for the estimation of cocaine in the 'total alkaloids.'

Cocaine $C_{17}H_{21}O_4N$ occurs to a variable extent in the different varieties of coca leaves (*see* above).

Preparation. The coca leaves are exhausted by maceration and agitation with a mixture of aqueous sodium carbonate and petroleum, whereby the cocaine with cinnamyl cocaine, &c., passes into solution in the petroleum. The latter is shaken with dilute hydrochloric acid, when cocaine hydrochloride crystallises out and is collected, pressed, and dried. This crude salt is purified by solution in water, liberation of the free base by ammonia and solution of this in alcoholic hydrogen chloride, when the hydrochloride crystallises out. The mother-liquors contain the other coca alkaloids. If Java coca leaves are used the coca alkaloids other than cocaine alone are obtained, and these and the residual coca alkaloids referred to above are converted into cocaine by heating with boiling hydrochloric acid and pouring into water, when truxillic acids separate and may be filtered off. The filtrate is concentrated until ecgonine hydrochloride crystallises out. The ecgonine is recovered, and then benzoylated and methylated in turn to produce cocaine.

The crude cocaine manufactured in Peru and imported to Europe for the preparation of cocaine salts is said to be obtained by extracting the leaves with 0·5 p.c. sulphuric acid, making the filtrate alkaline with sodium carbonate and extracting with petroleum. The latter is again shaken out with dilute sulphuric acid and the crude alkaloid precipitated from this as a white, bulky powder by sodium carbonate. The powder is washed with water and dried by exposure to air for export.

Properties. Monoclinic prisms, m.p. 98°; at higher temperatures it sublimes with decomposition. Lævorotatory $[\alpha]_D -15·8°$; slightly soluble in cold water, more soluble in hot water. Readily soluble in alcohol, ether, benzene, light or heavy petroleum, or carbon disulphide. The aqueous solution is alkaline to litmus, has a bitter taste, and produces a tingling and numbness of the tongue and lips, or, more generally, local anæsthesia of the surface to which it is applied. On this account it is largely employed in minor surgical operations, although in recent years it has been replaced to some extent by synthetically prepared anæsthetics, such as eucaine, stoväine, novocaine, &c. The alkaloid also causes dilatation of the pupil of the eye, but is not so powerfully mydriatic as some of the solanaceous alkaloids. When administered internally in small doses it acts as a stimulant, and diminishes the feeling of fatigue consequent on muscular exertion. Coca leaves have long been known to possess this property, and in places where the plant is abundant a mixture of lime and coca leaves is chewed by the natives before engaging in severe exertion. Larger doses of the alkaloid are poisonous.

The ordinary salts of cocaine are crystalline. The hydrochloride B·HCl, which is used in medicine, has m.p. 189·9°, and crystallises anhydrous from alcohol, or with $2H_2O$ from water. The chromate $B·H_2CrO_4,H_2O$ is thrown down as a pale-yellow precipitate when potassium chromate is added to an acid solution of the hydrochloride. This salt is very slightly soluble in cold water, m.p. 127°. The aurichloride $B·HAuCl_4$ is crystalline and sparingly soluble in water. When aqueous mercuric chloride is mixed with a solution of cocaine hydrochloride a bulky precipitate of the mercurichloride $B·HCl·HgCl_2,2H_2O$ is formed. This salt may be crystallised from alcohol, m.p. 124°.

d-Cocaine was obtained by Liebermann and Giesel (Ber. 1890, 23, 508, 926) from coca leaves, but was probably formed by the racemisation of *l*-cocaine by the action of alkalis; it has been synthesised from *d*-ecgonine. *dl*-Cocaine, m.p. 80°, was prepared from *dl*-ecgonine by Willstätter and Bode (*ibid.* 1901, 34, 1457).

Detection. In isolating cocaine the aqueous solution should not be heated for any length of ime, and not at all in presence of acids or lkalis. For the liberation of the alkaloid from ts salts, ammonia, and not caustic alkalis, should e employed. Cocaine may be detected by its haracteristic action on the tongue (*see* above). The following reactions are useful for the detection of the alkaloid: One c.c. of a 3 p.c. solution f potassium permanganate gives a violet preipitate with 0·01 grm. of the hydrochloride lissolved in two drops of water (Chem. Zeit. 886, 10, 71). The hydrochloride heated with lcoholic potash gives off an odour of methyl enzoate. Schaefer has suggested (J. Amer. Chem. Soc. 1899, 21, 634) that the differences n solubility of the chromates might be used for he detection of amorphous coca alkaloids in ocaine and its salts. The purity of cocaine ydrochloride may be roughly gauged by Maclagan's test (*cf.* B. Ph. G. 1899, 9, 38), which consists in dissolving 0·06 grm. of the ydrochloride in 60 grms. of water and adding 2 drops of 10 p.c. ammonia solution. A crystalline precipitate indicates that the hydrochloride s reasonably free from amorphous alkaloids, whilst a milky precipitate indicates the presence f amorphous coca bases.

REACTIONS AND CONSTITUTION. Cocaine exhibits most of the general reactions of the vegetable alkaloids. When boiled with water t is gradually hydrolysed into methyl alcohol and *benzoylecgonine* (*see* below)

$$C_{17}H_{21}O_4N+H_2O=C_{16}H_{19}O_4N+CH_3OH$$

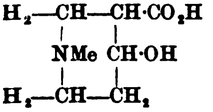
Paul, Pharm. J. 1887–1888, [iii.] 18, 781; Einhorn, Ber. 1888, 21, 47), and the same hange gradually occurs if the alkaloid remains n contact with an alkaline liquid. With alkalis r mineral acids methyl alcohol and benzoylcgonine are first formed, but the latter undergoes further hydrolysis into *benzoic acid* and *cgonine* (*see* below)

$$C_{17}H_{21}O_4N+2H_2O$$
$$=CH_3OH+C_7H_6O_2+C_9H_{15}O_3N.$$

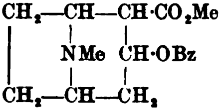
Natural cocaine is therefore methylbenzoyl-*l*-cgonine.

l-Ecgonine $C_9H_{15}O_3N$. This base does not ccur as such in coca leaves, but is the ultimate asic product of hydrolysis of cocaine, cinnamylocaine, the truxillines and benzoylecgonine. t crystallises from dry alcohol in monoclinic risms with $1H_2O$, m.p. 140°, or 198°–199° anhydrous); lævorotatory. It is readily esteried by alcohols yielding a series of alkyl esters, nd by acid chlorides or anhydrides, giving the cylecgonines from which the corresponding cocaines' are obtained by alkylation.

Ecgonine is now known, principally as the esult of the researches of Einhorn, Liebermann, Willstätter and their collaborators (*see* below), be closely related to tropine, the ultimate asic hydrolytic product of atropine and yoscyamine (p. 636), and may be regarded as opine-β-carboxylic acid. Ecgonine and its ost important derivative *l*-cocaine may be presented by the following formulæ:—



Ecgonine.



Cocaine.

Some of the chief papers bearing on the constitution of ecgonine are: Einhorn, Ber. 1889, 22, 399; 1890, 23, 1338; 1893, 26, 324; 1894, 27, 2823; Annalen, 1894, 280, 96; Liebermann, Ber. 1890, 23, 2518; 1891, 24, 606; Willstätter, *ibid.* 1897, 30, 702; 1898, 31, 1546, 2500, 2655; 1901, 34, 519; Annalen, 1903, 326, 79.

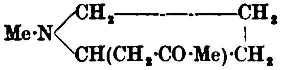
***l*-Benzoylecgonine** $C_{16}H_{19}O_4N$ is the first product of the hydrolysis of cocaine; it occurs in coca leaves from which it was isolated almost simultaneously by Skraup (Monatsh. 1885, 6, 556), and by Merck (Ber. 1885, 18, 1594). The base crystallises from water in needles, m.p. 86° (anhydrous 195°), and is hydrolysed by hydrochloric acid to benzoic acid and ecgonine. On methylation it furnishes cocaine.

***l*-Cinnamylcocaine** $C_{19}H_{23}O_4N$. This alkaloid is now known to occur in all varieties of coca leaves, but is found in largest proportion in the Java leaves, whence it was isolated by Giesel (Pharm. Zeit. 1889, 34, 516). It forms needles, m.p. 121°, from benzene on addition of light petroleum. Lævorotatory. On hydrolysis it furnishes cinnamic acid, methyl alcohol, and *l*-ecgonine, and is therefore methylcinnamyl-*l*-ecgonine. The *d*-isomeride has been prepared (Einhorn and Deckers, Ber. 1891, 24, 7).

Truxillines $C_{38}H_{46}O_8N_2$. Two of these, *α*- and *β*-, occur in coca leaves; the former is methyl-*α*-truxillyl-*l*-ecgonine, and the second the corresponding *β*-truxillyl compound (Hesse, Pharm. Zeit. 1887, 32, 407, 668; Liebermann, Ber. 1888, 21, 2342; 1889, 22, 130, 680). They are amorphous, and, according to von Liebrich, are heart poisons, and exert no local anæsthetic action.

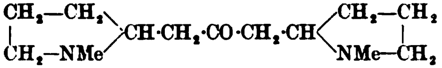
Tropacocaine (*Benzoylpseudotropeïne*) $C_{15}H_{19}O_2N$ was isolated by Giesel (Ber. 1891, 24, 2336) from Java coca leaves. It crystallises from ether, has m.p. 49°, is optically inactive, and distils unchanged. The salts are crystalline; the aurichloride has m.p. 208°. On hydrolysis tropacocaine furnishes benzoic acid and pseudotropine (Liebermann, *ibid.* 1891, 24, 2336, 2587; 1892, 25, 927); the latter is a physical isomeride of tropine (p. 636), and has been synthesised by Willstätter (Ber. 1896, 29, 936; 1901, 34, 129, 3163), who assigns to it the same structural formula as to tropine, and states that since tropine and pseudotropine are optically inactive the isomerism appears to be of the *cis-trans* type, a view subsequently confirmed by Barrowcliff and Tutin (Chem. Soc. Trans. 1909, 95, 1970). Tropacocaine, like the pseudotropeines as a class, is almost devoid of mydriatic action, but like cocaine (p. 646) is a local anæsthetic, though the effect is more transitory.

Hygrines. These secondary alkaloids were discovered by Lossen in Peruvian coca leaves (Annalen, 1862, 121, 374; 1865, 133, 352), and investigated by Liebermann and collaborators (Ber. 1889, 22, 675; 1891, 24, 407; 1893, 26, 851; 1895, 28, 578; 1896, 29, 2050; 1897, 30, 1113), who showed that Lossen's supposed homogeneous material contained two liquid alkaloids, one boiling at 193°–195° and having the formula $C_8H_{15}ON$, which makes it isomeric with tropine (p. 636), and a second having the composition $C_{14}H_{24}ON_2$, b.p. 215°, under 50 mm. pressure. The low boiling alkaloid is that now known as hygrine. Willstätter and Ettlinger's synthesis of hygrinic acid shows that hygrine probably has the following constitution (Annalen, 1903, 326, 91):—



Hygrine (Willstätter and Ettlinger).

From "cusco" leaves Liebermann and Cybulski isolated a third substance of this type, viz. cuscohygrine $C_{13}H_{24}ON_2$, b.p. 185° under 32 mm. pressure, which forms a crystalline hydrate $B,3\frac{1}{2}H_2O$, m.p. 40°. It probably has the constitution (L. a. C. Ber. 1895, 28, 578)—



Codeine. *See* under *Morphine* (p. 658).

Colchicine $C_{22}H_{25}O_6N$, an alkaloid existing in the seeds of the 'autumn crocus,' *Colchicum autumnale* (Linn.); *see* also COLCHICUM, vol. ii. p. 111.

Properties. A yellowish varnish, soluble in water, alcohol, or chloroform. It unites with chloroform forming a crystalline compound $B,2CHCl_3$. Lævorotatory. The aqueous solution has a very bitter taste. Colchicine is poisonous, causing death by vaso-motor paralysis (Dixon and Malden, J. Physiol. 1908, 37, 50). The alkaloid dissolves in sulphuric acid, forming a yellow solution, which becomes green, violet, and finally red on the addition of a drop of nitric acid. It contains three methoxyl groups and one acetyl group, and when treated with hydrochloric acid gives 3 mols. methyl chloride, 1 mol. acetic acid, and 1 mol. colchicinic acid $C_{15}H_{11}N(OH)_3COOH$. When heated with hydriodic acid colchicine furnishes one molecular proportion of methyl iodide, together with *colchiceine* $C_{21}H_{23}O_6N$, an alkaloid, which also occurs in *Colchicum autumnale* (Linn.). When a solution of colchicine is boiled with dilute sulphuric acid colchiceine and methyl alcohol are formed. Colchiceine crystallises with $\frac{1}{2}H_2O$, and melts at 139° or 172° (anhydrous). It is lævorotatory. Unlike colchicine, colchiceine is not poisonous (*cf.* Fühner Arch. expt. Pharm. 1913, 72, 228). Colchicine may be reproduced from colchiceine by heating it with methyl iodide and a solution of caustic soda in methyl alcohol (Zeisel, Monatsh. 1886, 7, 568; 1888, 9, 4, 868). According to Windaus colchicine is an enol methyl ether of colchiceine (Chem. Soc. Abstr. 1911, 100, i. 904), and may be represented by the formula

$$C_6H(OMe)_3{:}C_{10}H_8O(OMe)NH{\cdot}COMe.$$

Columbamine $C_{21}H_{21}O_5N$ occurs in calumba root (*Jateorrhiza columba* [Miers]) (vol. i. p. 615) along with *jateorrhizine* $C_{20}H_{19}O_5N$, and a third alkaloid *palmatine*. Columbamine is only known in the form of its salts which are all yellow. On reduction the hydriodide yields the colourless tetrahydrocolumbamine hydriodide (Günzel, Arch. Pharm. 1906, 244, 257). Columbamine contains a —OH and four —OMe groups. On methylation it furnishes a methylcolumbamine identical with the dimethyl ether similarly obtained from jateorrhizine, and this on oxidation with permanganate gives corydaldine (an oxidation product of corydaline) and 3 : 4 : 5-trimethoxy-*o*-phthalic acid (?), so that these two alkaloids are closely related to corydaline and berberine (Feist, *ibid.* 1907, 245, 586). Palmatine $C_{21}H_{21}O_6N$ is yellow, and on reduction yields a colourless tetrahydride; its relationship to its associates is unknown (Feist, *l.c.*). The statement frequently made that calumba root contains berberine is inaccurate (Gordin, *ibid.* 1902, 240, 146).

Conessine or **Wrightine** $C_{24}H_{40}N_2$ exists in *Wrightia antidysenterica* and in *Holarrhena africana* (A. DC.) and *H. antidysenterica* (Wall.). Crystals, m.p. 122° (Polstorff, Ber. 1886, 19, 78, 1682; Warnecke, *ibid.* 1886, 19, 60; Arch. Pharm. 1888, [iii.] 26, 248, 281).

Conhydrine (*Conydrine*). *See* under *Coniine*, below.

Coniceine. *See* under *Coniine*, below.

CONIINE AND THE ALKALOIDS OF HEMLOCK.

Coniine $C_8H_{17}N$ is one of several poisonous, volatile alkaloids found in hemlock, *Conium maculatum* (Linn.). A similar mixture of alkaloids occurs in fool's parsley (*Aethusa cynapium* [Linn.]) (Power and Tutin, J. Amer. Chem. Soc. 1905, 27, 146). Besides coniine, hemlock contains N-*methyl*-d-*coniine*, N-*methyl*-l-*coniine*, γ-*coniceine*, *conhydrine*, and *pseudoconhydrine*.

Preparation. Coniine is most readily separated from the crushed, unripe hemlock seeds by digesting them with water made alkaline with sodium carbonate, to decompose the coniine malate, and distilling the mixture in a current of steam. The distillate contains the coniine, together with much ammonia derived from the ammonium salts present in the seeds. The liquid is neutralised with hydrochloric acid and evaporated to dryness. The dry residue is extracted with absolute alcohol, when most of the ammonium chloride remains undissolved, whilst the alkaloidal hydrochlorides go into solution. If ether is added to the alcoholic solution a further quantity of ammonium chloride is separated. The residue left by the evaporation of the alcoholic solution is dissolved in cold water, ether added, and the coniine liberated by the addition of potash. The ethereal layer is decanted, washed, dried with potassium carbonate and distilled at a low temperature, when the coniine remains as an oily liquid. It may be purified from the accompanying conhydrine by fractional distillation: the coniine passes over first. So prepared the coniine contains γ-coniceine from which it may be freed by conversion into the hydrochlorides and extracting these when dry with acetone, in which the γ-coniceine salt is soluble and the coniine salt insoluble.

Properties. Colourless, alkaline liquid, having a remarkable, penetrating odour and a burning taste; b.p. 166°–167°, m.p. −2°; rel. den. 0·8626 at 0°, dextrorotatory $[\alpha]_D = +13{\cdot}79°$.

Coniine is slightly soluble in cold water, but less so in hot water, so that a clear, cold solution becomes turbid when warmed. It dissolves about one-quarter of its own volume of water at the ordinary temperature. When boiled with water the alkaloid distils with the steam. Coniine mixes with alcohol in all proportions, and is also readily soluble in ether, but only sparingly so in chloroform or carbon disulphide. Exposed in the air it darkens and slowly resinifies. When administered internally coniine acts as a powerful poison. It is a monacidic base.

The ordinary salts are crystalline and soluble in water or alcohol. The hydrochloride B·HCl forms rhombic crystals and melts at 220°. The aurichloride $B \cdot HAuCl_4$, m.p. 77°, forms minute yellow needles.

Reactions. Coniine is a strong base, which precipitates many metallic hydroxides from solutions of their salts.

It is a secondary amine. When oxidised with nitric acid it yields *normal butyric acid* among other products. When permanganate is used *a-pyridinecarboxylic acid* (*picolinic acid*) is obtained. On distillation with zinc-dust coniine is decomposed into hydrogen and *a-n*-propylpyridine.

Ladenburg has inferred from these and other reactions that coniine is a-propylpiperidine and has confirmed this by effecting the synthesis of the alkaloid by hydrogenating (with sodium in alcoholic solution) a-allylpyridine

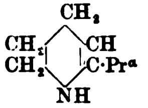
$$C_5H_4N(C_3H_5)+4H_2=C_5H_{10}N(C_3H_7).$$

The liquid thus produced possesses all the chemical and physical properties of the natural alkaloid except one; it is optically inactive (Ber. 1886, 19, 2579; 1906, 39, 2486). Ladenburg has also succeeded in resolving the inactive coniine into dextrorotatory and lævorotatory forms and has shown the dextro compound to be identical with the natural alkaloid. This was the first synthesis of a natural alkaloid.

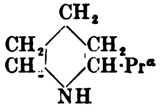
N-Methyl-*d*-coniine $C_8H_{16}(CH_3)N$ is stated to occur in hemlock (*v.* Planta and Kekule, Annalen, 1854, 89, 150), and remains with γ-coniceine when this is separated from coniine by fractional crystallisation of the acid tartrates. It has been synthesised by methylating coniine with potassium methyl sulphate (Wolffenstein, Ber. 1894, 27, 2611; *cf.* Passon, *ibid.* 1891, 24, 1678). It is a colourless, oily liquid, b.p. 173°–174°, closely resembling coniine.

N-methyl-*l*-coniine was obtained by Ahrens (*ibid.* 1902, 35, 1330) from residues accumulated in the preparation of coniine.

Coniceines. This name has been applied to a series of isomeric bases, $C_8H_{15}N$, obtained in various ways from the hemlock alkaloids. Only one of them γ-coniceine (2-propyl-Δ′-tetrahydropyridine) occurs in hemlock and was isolated from crude coniine obtained therefrom by Wolffenstein (Ber. 1895, 28, 302). This base was first prepared by Hofmann by the action of alkalis on bromoconiine. It strongly resembles coniine in odour and appearance, boils at 171°–172° under 746 mm. pressure, yields crystalline salts, and furnishes coniine on reduction. It has the constitution



γ-Coniceine.



Coniine.

Cf. Hofmann, Ber. 1885, 18, 16, 27, 112; Lellmann, Annalen, 1890, 259, 127; Löffler and colleagues, Ber. 1909, 42, 94, 107, 116, 124, 948, 3420; Gabriel, *ibid.* 1909, 42, 4059.

Conhydrine $C_8H_{17}ON$, also found in hemlock, may be separated from coniine with which it occurs either by cooling the concentrated ethereal solution of the two alkaloids, when the conhydrine crystallises out, or it may be obtained by distilling the crude coniine, when it remains behind in the retort, if the temperature has not exceeded 180°.

Conhydrine is a crystalline, basic substance, m.p. 121°, b.p. 226°, $[a]_D+10°$. On reduction it furnishes a mixture of coniceines (*see* above). According to Willstätter it is 2 : β-hydroxypropylpiperidine (Ber. 1901, 34, 3166; cf., however, Löffler and Tschunke, *ibid.* 1909, 42, 929).

Pseudoconhydrine $C_8H_{17}ON$, which is also found in hemlock, closely resembles conhydrine. It is a crystalline, strongly basic substance, m.p. 105°–106°; b.p. 236°. It is a secondary base and forms crystalline salts (Ladenburg and Adam, Ber. 1891, 24, 1671). Engler and Baur regard it as 2 : a-hydroxypropylpiperidine (*ibid.* 1894, 27, 1777), and Löffler has suggested that it is 4-hydroxy-2-propylpiperidine (*ibid.* 1909, 42, 116).

Conquinamine. *See* under *Quinine* (p. 673).

Cornutine. *See* under *Ergotoxine* (p. 653).

CORYDALINE AND THE CORYDALIS ALKALOIDS.

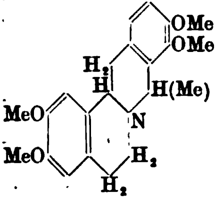
These alkaloids occur in the roots of *Corydalis tuberosa* (DC.). Certain of them possess a narcotic action, but they are not used in medicine, though corydalis tubers have been used as a drug. The chief alkaloids of the group are as follows:—

Corydaline $C_{22}H_{27}O_4N$,
Dehydrocorydaline $C_{22}H_{23}O_4N$,
Corybulbine $C_{21}H_{25}O_4N$,
*iso*Corybulbine $C_{21}H_{25}O_4N$.
Bulbocapnine $C_{19}H_{19}O_4N$,
Corytuberine $C_{19}H_{21}O_4N$,
Corydine $C_{20}H_{23}O_4N$,
*iso*Corydine $C_{20}H_{23}O_4N$.
Corycavine $C_{23}H_{23}O_6N$,
Corycavamine $C_{21}H_{21}O_5N$,
Corycavidine $C_{22}H_{25}O_5N$.

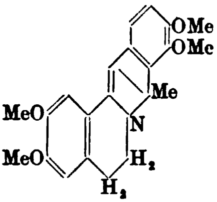
They fall naturally into 3 sub-groups of alkaloids closely related in chemical constitution and physiological action, and which may be called the corydaline, bulbocapnine, and corycavine sub-groups, as shown by the bracketing in the above table. According to Peters (Arch. expt. Path. Pharm. 1904, 51, 130) and Gadamer (Arch. Pharm. 1905, 243, 147) the corydaline sub-group produces paralysis of the spinal cord, the bulbocapnine sub-group gives rise to increased reflex action, whilst the corycavine sub-group stimulates the motor centres; all except corytuberine induce in frogs narcosis like that due to morphine. A method of isolation and separation of these alkaloids has been described by Gadamer, Ziegenbein and Wagner (Arch. Pharm. 1902, 240, 19).

Corydaline sub-group. The chief member *corydaline* $C_{22}H_{27}O_4N$ occurs in *Corydalis tuberosa* (DC.) and *C. ambigua* (Cham. and Schlecht.) (Makoshi, *ibid.* 1908, 246, 381). It crystallises from alcohol in hexagonal prisms, m.p. 134°–135°, $[a]_D^{16°}+300{\cdot}1°$ in chloroform, and furnishes well-crystallised salts; aurichloride $(B \cdot HCl)_2AuCl_3$, orange needles, m.p. 207°; platinichloride, m.p. 227°; ethyl sulphate $B \cdot C_2H_5HSO_4$, large prisms, m.p. 152°. On oxidation with iodine in alcohol it yields *dehydrocorydaline*, which occurs with it in *Corydalis tuberosa* (Schmidt, Arch. Pharm. 1908, 246, 575), *C.*

ambigua, and possibly *C. Vernyi* (Makoshi, *ibid.* 1908, 246, 381, 401). On oxidation by permanganate it gives eventually a mixture of hemipinic and *meta*hemipinic acids, and with nitric acid *meta*hemipinic and pyridine-2 : 3 : 4 : 6-tetracarboxylic acids, and from these results, and a study of the intermediate oxidation products, Dobbie and Lauder have assigned the following constitutional formulæ to corydaline and dehydrocorydaline (Chem. Soc. Trans. 1902, 81, 145; 1903, 83, 605; *cf.* Haars, Arch. Pharm. 1905, 243, 165)—



Corydaline.



Dehydrocorydaline.

which bring these alkaloids into close relationship with tetrahydroberberine and berberine respectively (p. 639).

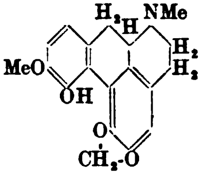
Corybulbine $C_{21}H_{25}O_4N$ crystallises in pale-yellow needles, m.p. 238°–240°, is dextrorotatory, $[\alpha]_D^{20}+303°$ (Bruns, *ibid.* 1903, 241, 634), and forms well-crystallised salts; the hydrochloride B·HCl forms yellowish prisms, m.p. 245°–250° (*l.c.*). On oxidation with iodine in alcohol corybulbine forms *dehydrocorybulbine* $C_{21}H_{21}O_4N$, m.p. 210°–211°, and on treatment with hydriodic acid furnishes 3 mols. methyl iodide. On methylation with methyl iodide in presence of potassium hydroxide it yields corydaline, so that it differs from the latter only in containing an —OH group in place of an —OMe group, probably in the *iso*quinoline nucleus (Dobbie and Lauder, Chem. Soc. Trans. 1895, 67, 25; and with Paliatseas, *ibid.* 1901, 79, 87).

*iso*Corybulbine $C_{21}H_{25}O_4N$, first obtained by Gadamer, Zeigenbein and Wagner (Arch. Pharm. 1902, 240, 19), crystallises in voluminous leaflets, m.p. 179°–180°, $[\alpha]_D+299·8°$, and on oxidation with iodine in alcohol yields *dehydro-isocorybulbine* $C_{21}H_{21}O_4N$, which resembles dehydrocorydaline and dehydrocorybulbine. The alkaloid contains three methoxyl groups (*cf.* Bruns, *ibid.* 1903, 241, 634).

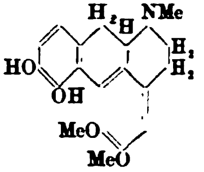
Bulbocapnine sub-group. The typical member of this group bulbocapnine $C_{19}H_{19}O_4N$ first obtained by Freund and Josephi (Annalen, 1893, 277, 10) separates from alcohol in rhombic needles, m.p. 199°, $[\alpha]_D+237·1°$ in chloroform, and yields crystalline salts. Bulbocapnine has until recently been regarded as a demethylated corydaline thus—

$C_{18}H_{15}(OMe)_4N$	$C_{18}H_{13}(OMe)(OH)_3N$
Corydaline.	Bulbocapnine.

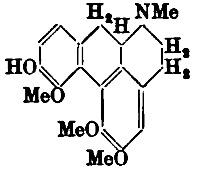
There was, however, very little evidence for this view, and Gadamer and Kuntze have shown that the alkaloid does not contain three OH groups. The oxygen atoms are present as methoxyl, hydroxyl, and dioxymethylene respectively. Further, 'exhaustive methylation' gives rise to 3 : 4-dimethoxy-5 : 6-dioxymethylene-8-vinylphenanthrene, which brings bulbocapnine into close relationship with apomorphine (p. 657). The same authors have investigated the other members of this group, and assign the following formulæ to the four alkaloids concerned (Arch. Pharm. 1911, 249, 503, 598, 641):—



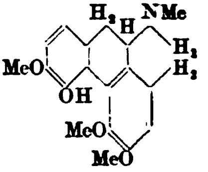
Bulbocapnine.



Corytuberine.



Corydine.



iso-Corydine

Corytuberine $C_{19}H_{21}O_4N$ crystallises with $5H_2O$ in colourless leaflets, m.p. 240°, $[\alpha]_D^{20°}+282·6°$, in alcohol and yields crystalline salts (Dobbie and Lauder, Chem. Soc. Trans. 1893, 63, 485; and Gadamer, Arch. Pharm. 1902, 240, 81; 1911, 249, 503, 641). *Corydine* $C_{20}H_{23}O_4N$ (crystals, with ½EtOH, m.p. 124°–125°, 149° anhydrous) has been described by Merck, and later by Gadamer, Ziegenbein and Wagner (*ibid.* 1902, 240, 81; 1911, 249, 669). On methylation with diazomethane corytuberine yields corydine and *iso*corydine (crystals, m.p. 185°, $[\alpha]_D^{20°}+195·3°$ in chloroform). The constitutional formulæ assigned by Gadamer (*l.c.*) to these three bases are given above.

Corycavine sub-group. The typical member of this group Corycavine $C_{23}H_{23}O_6N$, first obtained by Freund and Josephi (Annalen, 1893, 277, 15), crystallises in rhombic tablets, m.p. 218°–219°, and is optically inactive; it contains a dioxymethylene, but no ·OH or ·OMe group (Ziegenbein, Arch. Pharm. 1896, 234, 523; and Gaebel, *ibid.* 1910, 248, 207).

Corycavamine $C_{21}H_{21}O_5N$ is crystalline, m.p. 147°–148°, $[\alpha]_D^{20°}+166·6°$ in chloroform, and yields crystalline salts (Gadamer, Ziegenbein and Wagner, *ibid.* 1902, 240, 81).

Corycavidine $C_{22}H_{25}O_5N$, belonging to this sub-group, has been described by Gadamer (*ibid.* 1911, 249, 30). It is crystalline, has m.p. 212°–213°, $[\alpha]_D^{20°}+203·1°$ in chloroform, and, like corycavamine, is converted into the inactive form on heating at its melting-point. It appears to be corycavamine, in which a dioxymethylene group is replaced by two methoxyl groups.

Other alkaloids, including glaucine (p. 653) and protopine (p. 665) derived from *Corydalis* spp. have been referred to by Gadamer and others, *l.c.* and Arch. Pharm. 1911, 249, 224, 680; Haars, *ibid.* 1905, 243, 154; Makoshi, *ibid.* 1908, 246, 381, 401; Heyl, Apoth. Zeit. 1910, Nos. 5 and 17.

Cryptopine $C_{21}H_{23}O_5N$ occurs in opium, and is found in commercial papaverine; hexagonal prisms or plates, m.p. 218°, optically inactive, the aurichloride, m.p. 205° (decomp.), and the picrate, m.p. 215°, are crystalline; gives a bluish-violet coloration with sulphuric acid.

Exerts a narcotic action in small doses, but large doses paralyse the central nervous system (T. and H. Smith, Pharm. J. 1867, [ii.] 8, 595, 716; Pictet and Kramers, Ber. 1910, 43, 1329; Danckwortt, Arch. Pharm. 1912, 250, 590).

Cupreine. *See* under *Quinine* (p. 673).

Curarine. The drug known as 'curare' is a dry aqueous extract prepared from various species of *Strychnos*, indigenous in South America, where it was used by the natives as an arrow poison. Three kinds have appeared in commerce, viz. 'tube curare' in bamboo tubes, 'calabash curare' in small gourds, and 'pot curare' in unbaked clay jars. The first, also known as 'Para curare,' alone comes into commerce now, *v.* also vol. ii. 178. The drug has been examined by Roulin and Boussingault (Berz. J. 1829, 216), Buchner (*ibid.* 1861, 767), Preyer (*ibid.* 1865, 455), and Sachs (Annalen, 1878, 191, 254), who agree in stating that the intensely poisonous action is due to a basic substance, though they disagree as to whether this is amorphous or crystalline. Boehm (Arch. Pharm. 1897, 235, 660) has examined all three varieties of curare, and the following is a brief summary of his results :—

'TUBE CURARE.' This yields *tubocurarine* $C_{19}H_{21}O_4N$, an amorphous, bitter, intensely poisonous substance, and *curine* $C_{18}H_{19}O_3N$, a crystalline substance, m.p. 212°, crystallised from methyl alcohol, which is comparatively inactive physiologically.

Buraczewski and Zbijewski (Bull. Acad. Sci. Crac. 1910, 352) point out that these two bases give characteristic precipitates with iodine.

'CALABASH CURARE' yields *curarine*

$$C_{19}H_{26}ON_2,$$

which is amorphous, bitter, and poisonous.

'POT CURARE' furnishes *protocurarine* $C_{19}H_{23}O_2N$, poisonous; *protocurine* $C_{20}H_{23}O_3N$, crystalline, m.p. 306°, slightly toxic, and *protocuridine* $C_{19}H_{21}O_3N$, also crystalline, m.p. 275°, but physiologically inactive.

Curare is usually employed as such. It paralyses the motor nerve endings without, however, impairing the excitability of muscle, and on this account is largely employed in physiological research (*cf.* Edmund and Roth, Amer. J. Physiol. 1908, 23, 28, 46). *Delphocurarine* (*see* under *Delphinine*, below) exerts a similar action.

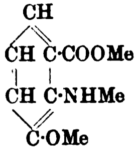
Cusconine $C_{23}H_{26}O_4N_2$, isomeric with aricine, which it accompanies in cusco bark (*Cinchona pubescens*). Crystals, m.p. 110° (Hesse, Annalen, 1877, 185, 301).

Cusparine $C_{19}H_{17}O_3N$ is found with *galipine* $C_{20}H_{21}O_3N$, *cusparidine* $C_{19}H_{17}O_3N$, *cuspareine* $C_{18}H_{13}N(OMe)_2$, *galipidine* $C_{19}H_{19}O_3N$, and *galipoidine* $C_{19}H_{15}O_4N$ in angostura bark (*Cusparia febrifuga*) [Hamb.]. Needle-shaped crystals, m.p. 90°–91°, or 110°–122°. Moderately soluble in ether, very soluble in alcohol (Körner and Böhringer, Gazz. chim. ital. 1883, 13, 363; Beckurts and Nehring, Arch. Pharm. 1891, 229, 591; Beckurts and Frerichs, Apoth. Zeit. 1903, 18, 697; Arch. Pharm. 1905, 243, 470; Tröger and others, *ibid.* 1910, 248, 1; 1911, 249, 174; 1912, 250, 494; 1913, 251, 246). *See* also CUSPARIA BARK, vol. ii. 180.

Cynoctonine. *See* under *Aconitine* (p. 634).

Cytisine $C_{11}H_{14}ON_2$ is contained in laburnum (*Cytisus Laburnum* [Linn.]), *Ulex europæus* (Linn.), *Sophora* spp., *Baptisia tinctoria* (R.Br.), *Euchresta Horsfieldii* (Benn.), and *Anagyris fœtida* (Linn.), from which it has been isolated under various names: ulexine, sophorine, baptitoxine (Husemann, Zeitsch. Chem. 1869, 5, 677; Gerrard, Pharm. J. 1886–87, [iii.] 17, 101, 229; Partheil, Ber. 1890, 23, 3201; 1891, 24, 634; Buchka and Magalhaës, *ibid.* 1891, 24, 253, 674). Prisms, m.p. 153°, which sublime without decomposition. Soluble in water, alcohol, or chloroform, insoluble in light petroleum. Cytisine usually behaves as a diacidic base: salts crystalline. The aurichloride $B{\cdot}HAuCl_4$ melts at 220°. In aqueous solution cytisine is lævorotatory, $[\alpha]_D^{17°} = -120°$, and gives with ferric chloride a red coloration, which is discharged by a few drops of aqueous hydrogen peroxide, a blue coloration being subsequently observed. Cytisine is a violent poison. For recent work on the chemistry of cytisine, *see* Freund and others, Ber. 1901, 34, 615; 1904, 37, 16; 1906, 39, 814; Maass, *ibid.* 1908, 41, 1635; Ewins, Chem. Soc. Trans. 1913, 103, 97. *Caulophyllum thalictroides* (Linn.) contains methylcytisine (Power and Salway, Chem. Soc. Trans. 1913, 103, 194).

Damascenine $C_{10}H_{13}O_3N$ occurs in the seed-coats of *Nigella damascena* (Linn.) and *N. arvensis* (Linn.). Crystalline mass, m.p. 26°, b.p. 270° under 750° mm. pressure. The solutions show blue fluorescence. The salts crystallise well. The alkaloid is narcotic. On treatment with acids or alkalis damascenine is hydrolysed into methyl alcohol and damasceninic acid, m.p. 144°, which with hydriodic acid yields 2-methylamino-3-hydroxybenzoic acid and methyl iodide, so that damasceninic acid appears to be 2-methylamino-3-methoxybenzoic acid, and damascenine itself is probably represented by the following formula :—



(Schneider, Pharm. Centh. 1890, [ii.] 173; Pommerehne, Arch. Pharm. 1899, 237, 475; 1900, 238, 531; 1904, 242, 295; Keller, *ibid.* 299; 1908, 246, 1; 1910, 248, 463 (Ewins, Chem. Soc. Trans. 1912, 101, 544).

Daucine $C_{11}H_{1}$[illegible]N_2, colourless, oily base, b.p. 240°–250°, occurring in carrot leaves (Pictet and Court, Ber. 1907, 40, 3771).

Delphinine $C_{31}H_{49}O_7N$ is one of a series of ill-defined alkaloids, including *delphisine*, *delphinoidine*, *staphisagroine*, and *staphisagroidine*, found in stavesacre seeds (*Delphinium Staphisagria* (Linn.)). (Kora-Stojanoff, Chem. Zentr. 1890, [ii.] 628, and Ahrens, Ber. 1899, 32, 1581, 1669.) *Delphinium consolida* and *D. ajacis*, according to Keller (Arch. Pharm. 1910, 248, 468; 1913, 251, 207), also contain alkaloids. From various *Delphinium* spp. Heyl has obtained 'delphocurarine,' an amorphous mixture of bases, including a crystalline substance, m.p. 184°–185° (Chem. Soc. Asbtr. 1903, i. 650).

'Delphocurarine' resembles curarine (*see* above) in physiological action (Lohmann, Pflug. Arch. 1902, 92, 398).

Dicentrine $C_{20}H_{21}O_4N$ occurs with protopine in *Dicentra pusilla* (Sieb. and Zucc.) and possibly in *D. formosa* (Walp.). Prismatic crystals, m.p. 168°–169°, $[\alpha]_D + 62°$ in chloroform. Salts crystalline (Heyl, Arch. Pharm. 1903, 241, 313; Asahina, *ibid.* 1909, 247, 201). Produces slight narcosis (Iwakawa, Arch. expt. Path. Pharm. 1911, 64, 369). Gadamer has stated (Arch. Pharm. 1911, 249, 680) that dicentrine resembles glaucine in its properties, and suggests that it is glaucine (p. 653) in which the two —OMe groups in positions 5 and 6 are replaced by a dioxymethylene group.

Dioscorine, $C_{13}H_{19}O_2N$, greenish-yellow plates, m.p. 43·5°, occurs in *Dioscorea hirsuta* (Blume) tubers. Bitter and poisonous (Gorter, Rec. Trav. Chim. 1911, 30, 161).

Ecgonine. *See* under *Cocaine* (p. 647).

EMETINE AND THE ALKALOIDS OF IPECACUANHA.

Emetine $C_{30}H_{44}O_4N_2$ occurs with *cephaeline* $C_{25}H_{40}O_4N_2$ and *psychotrine* in ipecacuanha root (*Psychotria Ipecacuanha*), (Stokes) which contains up to 2·5 p.c. of total alkaloids.

Preparation. The emetine may be extracted from ipecacuanha by moistening the finely-powdered root with ammonia and extracting with alcohol. From the total alkaloids so isolated emetine is separated by extraction with ether in presence of alkali.

Properties. Amorphous, colourless, m.p. 68°, yielding crystalline salts. In minute doses emetine produces local irritation resulting in emesis; in large doses it affects the central nervous system causing collapse and death.

Cephaeline $C_{25}H_{40}O_4N_2$ crystallises in colourless needles, m.p. 96°–102°, and exerts a physiological action similar to that of emetine.

Psychotrine is crystalline, m.p. 140°, and is physiologically inactive (Kunz-Krause, Arch. Pharm. 1887, 225, 461; 1894, 232, 466; Paul and Cownley, Pharm. J. 1894–1895, [iii.] 25, 373, 641, 690; Keller, Arch. Pharm. 1911, 249, 512).

DETECTION OF IPECACUANHA ALKALOIDS. The mixed ipecacuanha alkaloids have occasionally been mistaken for morphine. They may be distinguished by the fact that with Fröhde's reagent they give a violet coloration, changing to deep blue on addition of hydrochloric acid. Further, the alkaloidal residue from ipecacuanha readily develops microscopic crystals of psychotrine under the influence of ammonia gas (*cf.* Allen and Scott-Smith, Analyst, 1902, 27, 345).

ESTIMATION OF TOTAL ALKALOIDS IN IPECACUANHA. This is best accomplished, according to Flückiger, by extracting the finely-powdered root with boiling chloroform to which about 1 p.c. of aqueous ammonia has been added. Ransom finds it is better to exhaust the root with chloroform made alkaline with ammonia by shaking with aqueous ammonia and then withdrawing the layer of water. The solution in chloroform is shaken with dilute sulphuric acid, and the quantity of 'emetine' in the acid solution determined by titration with Mayer's solution (Pharm. J. 1887–1888, [iii.] 18, 241).

These processes were devised for the estimation of 'emetine' when the 'total alkaloid' of the root was regarded as consisting solely of emetine. Since Paul and Cownley have shown that the total alkaloids include three substances, emetine, cephaeline, and psychotrine, of which only the first two are active, these processes require some modification in order to give a correct idea of the medicinal value of the root. Frerichs and Fuentes Tapis (Arch. Pharm. 1902, 240, 390) and Keller (*ibid.* 1911, 249, 512) have employed ether in place of chloroform, since this extracts emetine and cephaeline, but not psychotrine (*cf.* U.S. Pharmacopeia, 8th ed.).

Ephedrine $C_{10}H_{15}ON$, crystals, m.p. 39°, b.p. 225°, occurs in *Ephedra vulgaris.* It is a secondary base, furnishes crystalline salts, and on 'exhaustive methylation' yields eventually trimethylamine and α-phenylallyl alcohol $C_9H_{10}O$. On distillation the hydrochloride furnishes methylamine and propiophenone. When heated with hydrochloric acid, ephedrine undergoes isomerisation to ψ-ephedrine (*iso*ephedrine), crystals, m.p. 117°, which also occurs with it in *E. vulgaris.* Both bases are poisonous and ephedrine hydrochloride has been used as a mydriatic (Ngai, Chem. Zentr. 1894, i. 470; Merck's Bericht, 1893, 13; Ladenburg and Oelschälgel, Ber. 1889, 22, 1823; Miller, Arch. Pharm. 1902, 240, 481; Flaecher, *ibid.* 1904, 242, 380; Schmidt and collaborators, *ibid.* 1905, 243, 73; 1906, 244, 239, 241, 269; 1908, 246, 210; 1909, 247, 141; 1911, 249, 305; 1913, 251, 320; Apoth. Zeit. 1911, No. 37; Fourneau, J. Pharm. Chim. 1904, [vi.] 20, 481; Emde, Arch. Pharm. 1907, 245, 662; Gadamer, *ibid.* 1908, 246, 566; Calliess, Apoth. Zeit. 1910, 25, 677). According to Rabe (Ber. 1911, 44, 824) the ammonium base of ephedrine decomposes into water, trimethylamine and α-phenylpropylene-αβ-oxide, and he regards ephedrine and ψ-ephedrine as optically isomeric β-methylamino-α-phenylpropane-α-ols $OH{\cdot}CHPh{\cdot}CHMe{\cdot}NHMe$ (*cf.* Emde, *l.c.*).

The name ephedrine has also been applied by Spehr to a crystalline alkaloid $C_{13}H_{19}ON$, m.p. 112°, obtained from *Ephedra monostachya*, a drug used as a remedy for syphilis and gout in Bessarabia and Wallachia. Ordinary ephedrine is known commercially as 'ephedrine (Merck)' and the second species as 'ephedrine (Spehr).'

ERGOTOXINE AND THE ALKALOIDS OF ERGOT.

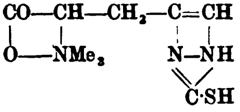
Commercial ergot consists of the mycelia of the fungus *Claviceps purpurea*, which occurs on rye and occasionally on other cereals. It is of considerable importance owing to its use in obstetric medicine, and to the fact that chronic poisoning due to the use of rye grain containing ergot as food was at one time not uncommon. Much confusion has been introduced into the chemistry of ergot by the characterisation of impure substances, often merely by physiological tests, but this has now largely disappeared as a result of the work done by Barger and collaborators, Kraft, Kutscher, and others, who have corrected and largely extended the pioneer work done by Tanret in 1875–1878. It is now known with certainty that ergot contains a crystalline, but physiologically inert, alkaloid *ergotinine*, an amorphous alkaloid *ergotoxine* (hydroergotinine), and a series of physiologically active amino acids, which appear to result mainly from putrefactive changes, and also occur in putrid flesh.

Ergotoxine $C_{35}H_{41}O_6N_5$ was first obtained in a pure state by Barger and Carr (Rept. Brit. Assoc. 1906, 526; Chem. News, 1906, 94, 89), and was fully described by them in 1907 (Chem. Soc. Trans. 1907, 91, 337). The same substance was obtained by Kraft independently in 1906 (Arch. Pharm. 1906, 244, 336) and called hydroergotinine, since it was converted into ergotinine by loss of 1 mol. H_2O. It seems clearly established that Tanret's 'amorphous ergotinine' (Compt. rend. 1875, 81, 896; 1878, 86, 888), and Jacobi's 'sphacelotoxine' (Arch. expt. Path. Pharm. 1897, 39, 104) consisted of impure ergotoxine, and that Kobert's 'cornutine' (*l.c.*) probably contained some ergotoxine. The alkaloid is a bulky, colourless, powder, m.p. 162°–164°, which shows varying dextrorotation. It gives colour reactions like those referred to under ergotinine (*see* below), and yields crystalline salts; the phosphate $B{\cdot}H_3PO_4,H_2O$, colourless needles, being that most easily obtained. On boiling with methyl alcohol (Kraft) or with acetic anhydride (Barger and Carr) ergotoxine is converted into ergotinine. On destructive distillation both ergotoxine and ergotinine yield *iso*butyrylformamide (Barger and Ewins, Chem. Soc. Trans. 1910, 97, 284). Ergotoxine produces in very small doses the effects characteristic of ergot, including gangrene (Barger and Dale, Bio-Chem. J. 1907, 2, 240; Dale, J. Physiol. 1913, 46, 291).

Ergotinine $C_{35}H_{39}O_5N_5$ was first isolated by Tanret (Compt. rend. 1875, 81, 896), who assigned to it the formula $C_{35}H_{40}O_6N_4$. The formula now accepted for the alkaloid $C_{35}H_{39}O_5N_5$ is due to Barger and Carr (Chem. Soc. Trans. 1907, 91, 337; *cf.* Tanret, J. Pharm. Chim. 1906, [vi.] 24, 397). Ergotinine crystallises in long, colourless needles, melts indefinitely at about 229° (corr.), has $[\alpha]_D^{10}$ +338° in alcohol, and does not give crystalline salts. Sulphuric acid with ergotinine in ether yields an orange coloration changing to blue, and ferric chloride produces a succession of colours—yellow, orange, crimson, green, dark blue—when added to a solution of the alkaloid in sulphuric acid. On standing in acetic acid at atmospheric temperature (Kraft) ergotinine is converted into ergotoxine. Ergotinine exercises little or no physiological activity (Barger and Dale, Arch. Pharm. 1906, 244, 554; *cf.* Kobert, Arch. expt. Path. Pharm. 1884, 18, 316).

Other Basic Constituents of Ergot.

Ergothioneine $C_9H_{15}O_2N_3S,2H_2O$, m.p. 290°, was obtained by Tanret (Compt. rend. 1909, 149, 222); it crystallises in colourless, monoclinic lamellæ. According to Barger and Ewins (Chem. Soc. Trans. 1911, 99, 2336) it is a thiolglyoxaline derivative of the following formula:—



A considerable number of amino bodies have been isolated from ergot from time to time, and recently several physiologically active substances of this kind have been prepared from the drug and characterised.

'**Clavine**' (Vahlen, Arch. expt. Path. Pharm. 1906, 55, 136; 1908, 60, 42), according to Barger and Dale (Bio-Chem. J. 1907, 2, 240), is a mixture of leucine and aspartic acid.

Aminosecalesulphonic acid

$$NH_2{\cdot}C_{15}H_{27}O_5{\cdot}HSO_3$$

(Kobert's 'ergotic acid'), obtained by Kraft (*l.c.*), is described by Vahlen (*l.c.*) as physiologically inactive.

p-**Hydroxyphenylethylamine** was shown by Barger (Chem. Soc. Trans. 1909, 95, 1123) to be present in ergot in small quantity, and to be responsible in part for the rise in blood pressure produced by aqueous extracts of ergot (Barger and Dale, Proc. Physiol. Soc. 1909). The same authors have shown that *iso*amylamine is probably present in ergot in minute quantity.

(4- or 5)-β-**Aminoethylglyoxaline** was isolated almost simultaneously from ergot by Kutscher (Z. P. 1910, 24, 163), and by Barger and Dale (Chem. Soc. Trans. 1910, 97, 2592), and shown to possess great physiological activity, producing marked contraction of the isolated uterus even when applied in very minute amounts (*cf.* Dale and Laidlaw, J. Physiol. 1910, 41, 318).

Agmatine (*aminobutyleneguanidine*)

$$NH_2{\cdot}C(NH)NH[CH_2]_4{\cdot}NH_2$$

was prepared from ergot by Engeland and Kutscher (Z. P. 1910, 24, 479); this also causes contraction of the isolated uterus and induces a rise in blood pressure.

Erythrophleine $C_{28}H_{43}O_7N$, an amorphous alkaloid found in sassy bark (*Erythrophleum guineense* (G. Don)). It resembles digitalin in physiological action (Gallois and Hardy, Bull. Soc. chim. 1876, 26, 39; Harnack, Chem. Zentr. 1897, [i.] 301).

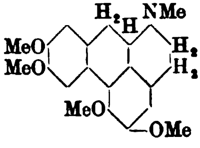
Eseramine. *See* under *Physostigmine* (p. 663).

Galipine and **Galipoidine.** *See* under *Cusparine* (p. 651).

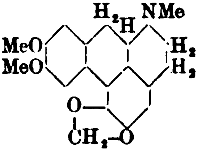
Gelsemine $C_{20}H_{22}O_2N_2$, a crystalline alkaloid occurring in the root of American wild jasmine *Gelsemium sempervirens*, (Ait.) along with gelseminine and a third alkaloid, the two latter being amorphous and yielding amorphous derivatives (Wormley, Amer. J. Pharm. 1870, 42, 1; Sonnenschein, Ber. 1876, 9, 1182; Gerrard, Pharm. J. 1882–1883, [iii.] 13, 502, 641; Thompson, *ibid.* 1886–1887, [iii.] 17, 805; Spiegel, Ber. 1893, 26, 1045; Cushny, *ibid.* 1725; Goeldner, B. Ph. G. 1895, 5, 330). The roots have been thoroughly re-examined by Moore (Chem. Soc. Trans. 1910, 97, 2223; 1911, 99, 1231).

Properties. Crystallises from acetone in handsome, glistening prisms containing 1 mol. of acetone, melts at 178°, and has $[\alpha]_D$ +15·9° in chloroform. The salts crystallise well, $B{\cdot}HCl$, m.p. 300°, small prisms; $B{\cdot}HNO_3$, m.p. 280°, glistening prisms. Gelsemine hydrochloride is physiologically inactive to mammals, but produces strychnine-like effects in frogs. The characteristic physiological action of gelsemium roots is due to the two amorphous alkaloids, to one of which the name 'gelseminine' has been applied. In general their physiological action resembles that of coniine; they are highly toxic and also exert a mydriatic action on the eye (Cushny, *l.c.*; Moore, *l.c.*).

Glaucine $C_{21}H_{25}O_4N$ occurs in *Glaucium flavum* (Crantz) along with protopine (Battandier, Chem. Soc. Abstr. 1892, 62, i. 893). Crystallises in rhombic prisms, m.p. 119°–120°, $[\alpha]_D$ +113·3° in alcohol, is a tertiary base and contains four ·OMe groups (Fischer, Arch. Pharm. 1901, 239, 426). It has been synthesised by Gadamer (*ibid.* 1911, 249, 680) and shown to be phenanthreno-N-methyltetrahydropapaverine, and therefore is closely related to dicentrine (p. 652).



Glaucine.



Dicentrine.

Glaucine is tasteless and induces narcosis, accompanied by some tetanising action.

Gnoscopine. *See Narcotine* (p. 659).

Guanine. *See* under *Caffeine* (p. 642).

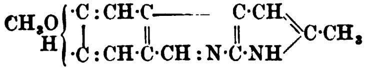
Guvacine. *See* under *Arecoline* (p. 635).

Harmaline $C_{13}H_{14}ON_2$ occurs along with *harmine* $C_{13}H_{12}ON_2$ and *harmalol* $C_{12}H_{12}ON_2$ as a phosphate in the seeds of *Peganum Harmala* (Linn) (Göbel, Annalen, 1841, 38, 363; Fritzsche, *ibid.* 1847, 64, 360; O. Fischer, Ber. 1885, 18, 400; 1889, 22, 637; 1897, 30, 2481; 1905, 38, 329; 1912, 45, 1930; Chem. Zentr. 1901, i. 957; and Hasenfratz, Compt. rend. 1912, 154, 215, 704, 1520).

Properties. Small tabular crystals, m.p. 238° (decomp.), $[\alpha]_D=0°$. Very slightly soluble in water, more soluble in alcohol or ether. A monacidic base; the salts are yellow, and their aqueous solutions exhibit a green fluorescence.

Reactions and constitution. On oxidation harmaline is converted into *harmine* $C_{13}H_{12}ON_2$, a crystalline alkaloid, m.p. 256°, also found in small quantity in peganum seeds. Its salts are colourless, but show a blue fluorescence in aqueous solution. Both harmaline and harmine contain one methoxyl group, and when heated with hydrochloric acid furnish methyl chloride harmalol $C_{12}H_{12}ON_2$ (m.p. 212°, slender red needles) and harmol $C_{12}H_{10}ON_2$ (m.p. 321°, greyish needles) respectively; ahrmalol also occurs in *Peganum* seeds. Oxidation with nitric acid converts harmine and harmol into harmic acid $C_{10}H_8O_6N_2$ and 1-methoxy-2-nitro-3:4-phthalic acid, whence it appears that this group of bases must contain the complex $OMe\cdot C_6H_3(C\cdot)C\cdot$ in which $\cdot OMe$, (C.), and C. occupy positions 1 : 3 : 4 or 1 : 4 : 5.

Perkin and Robinson (Chem. Soc. Trans. 1912, 101, 1775) have assigned the following formula to harmine:—



$$\begin{matrix}CH_3O\\H\end{matrix}\left\{\begin{matrix}\cdot C:CH\cdot C\text{———}\qquad C\cdot CH\\ |\qquad\quad \|\qquad\qquad\qquad \|\\ \cdot C:CH\cdot C\cdot CH:N\cdot C\cdot NH\end{matrix}\right.\!\!>C\cdot CH_3$$

Harmine and harmaline cause convulsions, increase of saliva, interference with respiration, and depression of temperature in warm-blooded animals (Gunn, T. E. 1910, 47, 245; Flury, Arch. expt. Path. Pharm. 1910, 64, 105). In Turkey peganum seeds are used as an anthelmintic, and Flury (*l.c.*) ascribes this action to the paralysis of the musculature of the parasites caused by harmaline.

Histidine $C_6H_9O_2N_3$, 4- (or 5-)glyoxaline-α-amino-propionic acid, occurs in various plant seedlings (Schulze, Zeitsch. physiol. Chem. 1899, 28, 465); needles or leaflets, m.p. 253°, $[\alpha]_D$ −39·74° (Kossel, Chem. Soc. Abstr. 1896, 70, 582). *V.* vol. iii. p. 41.

Homoquinine. *See Cupreine* (p. 673).

Hordenine $C_{10}H_{15}ON$ occurs in barley germs. Crystallises in orthorhombic prisms, m.p. 117·8°, sublimes at 140°–150°, b.p. 173°–174°/11 mm., is optically inactive, yields crystalline salts and behaves as a tertiary base. It has the constitution $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2[OH:CH_2 etc. = 1:4]$ (Léger, Compt. rend. 1906, 142, 108, 143; 234, 916; 1907, 144, 488; Gaebel, Arch. Pharm. 1906, 244, 435), and has been synthesised by Barger (Chem. Soc. Trans. 1909, 2193), and by Rosenmund (Ber. 1910, 43, 306). It is slightly toxic (Camus, Compt. rend. 1906, 142, 110, 237, 350). *V.* vol. iii. p. 46.

HYDRASTINE AND THE ALKALOIDS OF HYDRASTIS CANADENSIS.

Hydrastine $C_{21}H_{21}O_6N$, an alkaloid occurring together with berberine (*see* p. 639), and canadine in the root of *Hydrastis canadensis* (Linn.) to the extent of about 1·5 p.c.

Preparation and estimation. Hydrastine may be isolated from the mother-liquid from which the berberine salt has crystallised (p. 639). This is largely diluted with water, and almost neutralised with ammonia. On evaporation, ammonium sulphate, resin, &c., separate out; these are removed, and the hydrastine precipitated from the cold liquid by ammonia. The coloured precipitate is dissolved in alcohol, and the colouring matter removed by digestion with animal charcoal; the alkaloid crystallises from the concentrated solution. In order to purify it the hydrastine is repeatedly crystallised from alcohol.

According to Freund and Will (Ber. 1886, 19, 2797) hydrastine is most readily obtained by percolating finely-powdered hydrastis root with ether, and crystallising the ethereal residue from alcohol.

A method for the estimation of hydrastine and berberine separately in hydrastis rhizome has been proposed by Gordin and Prescott (Arch. Pharm. 1899, 237, 499; 1901, 239, 638).

Properties. Colourless, rhombic prisms, m.p. 132°. Insoluble in water; readily soluble in chloroform or benzene; less soluble in ether or alcohol. The alcoholic solution is alkaline to litmus and lævorotatory; in chloroform $[\alpha]_D = -67·8°$. The ordinary salts of hydrastine are soluble in water but do not crystallise well. They are poisonous to animals (Perrins, Pharm. J. 1861–1862, [ii.] 3, 546; Mahla, Amer. J. Sci. 36, 57; Lloyd, Proc. Am. Pharm. Assoc. 26, 805; Power, Pharm. J. 1884–1885, [iii.] 15, 297; 1885–1886, [iii.] 16, 1092; Schmidt and Kerstein, Arch. Pharm. 1890, [iii.] 28, 49).

Reactions. When permanganate is added to an acid solution of hydrastine sulphate in water a blue fluorescence is observed. Iodine solution gives a characteristic periodide. For other colour reactions of hydrastine, *see* Lyons, Pharm. J. 1885–1886, [iii.] 16, 880; and Labat, Bull. Soc. chim. 1909, [iv.] 5, 742, 745.

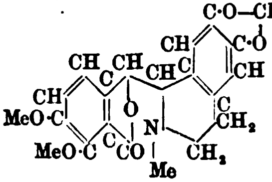
The principal products of the oxidation of hydrastine by nitric acid are opianic acid and hydrastinine $C_{11}H_{13}O_3N$, thus—

$$\underset{\text{Hydrastine.}}{C_{21}H_{21}O_6N}+H_2O+O=\underset{\text{Opianic acid.}}{C_{10}H_{10}O_5}+\underset{\text{Hydrastinine.}}{C_{11}H_{13}O_3N}.$$

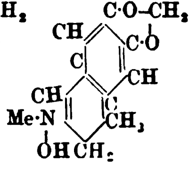
Opianic acid has the constitution

$$C_6H_2(OMe)_2(COOH)(CHO)$$
$$[OMe:OMe:COOH:CHO=1:2:3:4].$$

HYDRASTININE, m.p. 116°–117°, crystallises from light petroleum in glancing crystals easily soluble in alcohol or ether, sparingly in water. It is used in medicine as an internal styptic. On 'exhaustive methylation' hydrastinine gives trimethylamine and hydrastal $C_{10}H_8O_3$: the latter on oxidation gives hydrastic acid (4:5-dioxymethylenephthalic acid). These reactions indicate the following constitution for hydrastine and hydrastinine :—



Hydrastine.



Hydrastinine.

(*cf.* Freund, Annalen, 1892, 271, 320; Fritsch, *ibid.* 1895, 286, 18; Roser, *ibid.* 1889, 254, 357; Dobbie and Tinkler, Chem. Soc. Trans. 1904, 85, 1005).

Canadine $C_{20}H_{21}O_4N$ occurs with crude hydrastine (*see* above), from which it may be isolated by fractional crystallisation of the nitrates, the canadine salt being less soluble. Silky needles, m.p. 132·5° $[\alpha]_D - 298°$ in chloroform (Schmidt, Arch. Pharm. 1894, 232, 136). On treatment with iodine it is converted into berberine. By fractional crystallisation of tetrahydroberberine *d*-camphorsulphonate, Gadamer (*ibid.* 1901, 239, 648) isolated a lævorotatory base identical with canadine, which is therefore *l*-tetrahydroberberine. Jowett and Pyman have found *l*-α-canadine methochloride in *Xanthoxylum brachyacanthum*, Chem. Soc. Trans. 1913, 103, 293.

Hygrine. *See* under *Cocaine* (p. 647).

Hymenodictyonine (*Hymenodictine*) $C_{23}H_{40}N_2$, crystals, m.p. 66°, occurs in the bark of *Hymenodictyon excelsum* (Wall.), used in India as an antipyretic. It is bitter and slightly toxic (Naylor, Pharm. J. 1883, [iii.] 13, 817; 1885, [iii.] 15, 195).

Hyoscine. *See Scopolamine* (p. 639).

Hyoscyamine. *See* under *Atropine* (p. 637).

Hypaphorine $C_{14}H_{18}O_2N_2$, an alkaloid isolated from *Erythrina hypaphorus* (Boerl.) by Greshoff (Med. s'Lands Plant. 1890, 7, 29; Chem. Soc. Abstr. 1891, 60, 335), and subsequently investigated by van Romburgh (Proc. K. Akad. Wetenoch. Amst. 1911, 13, 1177), and by van Romburgh and Barger (Chem. Soc. Trans. 1911, 99, 2068), and shown to be α-trimethyl-β-indolepropiobetaine, since it is produced by the action of methyl iodide on trytophan (β-indole-α-aminopropionic acid) and treating the resulting methiodide with warm dilute alkali. Hypaphorine crystallises as a monohydrate, m.p. 255°, [α] +91·93°, and yields a sparingly soluble nitrate, m.p. 215°–220°. It exhibits no marked physiological action.

Hypoxanthine. *See* under *Caffeine* (p. 642).

Ibogäine $C_{26}H_{32}O_2N_2$ (*Ibogine*), an alkaloid occurring in 'iboga' obtained from the French Congo. Orthorhombic crystals, m.p. 152°, lævorotatory (Dybowski and Landrin, Compt. rend. 1901, 133, 748; Haller and Heckel, *ibid.* 1901, 133, 850). The alkaloid produces anæsthesia, and in large doses causes convulsions and death due to stoppage of respiration (Lambert and Heckel, *ibid.* 1901, 133, 1236).

Imperialine $C_{35}H_{59}O_4N$ (?) occurs in the bulbs of *Fritillaria Imperialis* (Linn.). Short needles, m.p. 254° (approx.), [α] −35·4° in chloroform; yields a crystalline hydrochloride. It slows the action of the heart (Fragner, Ber. 1885, 21, 3284).

Jaborine. *See* under *Pilocarpine* (p. 664).

Jateorrhizine. *See* under *Columbamine* (p. 648).

Jervine. *See* under *Cevadine* (p. 644).

Laudanidine and **Laudanine.** *See* under *Papaverine grout* (p. 661).

Laudanosine. *See* under *Papaverine* (p. 661).

Laurotetanine $C_{19}H_{23}O_5N$ occurs in the bark of *Litsea citrata* (Blume), and in many East Indian lauraceous plants (Greshoff, Ber. 1890, 23, 2546). It crystallises in needles, m.p. 134°, gives crystalline salts, behaves as a secondary amine, contains three ·OMe groups, and probably one hydroxyl group. It exerts a tetanising action in frogs, but is less powerful than strychnine (Filippo, Arch. Pharm. 1898, 236, 601).

Lobeline $C_{18}H_{23}O_2N$, the characteristic alkaloid of *Lobelia inflata*, (Linn.) a drug used as a remedy for spasmodic asthma. Amorphous, viscous, strongly alkaline liquid, soluble in alcohol, sparingly soluble in other solvents; it darkens and resinifies in light and air. The hydrochloride $B{\cdot}HCl,H_2O$, m.p. 129°, and the platinichloride $(B{\cdot}HCl)_2PtCl_4,3H_2O$ are crystalline (Siebert, Inaug. Diss. Marburg, 1891). The alkaloid is highly toxic, exercising in small doses a stimulating, and in large doses a paralysing action on the respiratory centre (Edmunds, Amer. J. Physiol. 1904, 11, 79).

Lophophorine. *See* under *Mezcaline* (p. 656).

Lupanine $C_{15}H_{24}ON_2$ occurs in the *d*- and *dl*-form in the seeds of *Lupinus albus* (Linn.), and in the *d*- form in those of *L. angustifolius* (Linn.) and *L. perennis* (Linn.) The *dl*- form crystallises in needles, m.p. 99°, and furnishes crystalline salts. The *d*- form has m.p. 44°, and yields salts which are less soluble and crystallise more easily than those of the *dl*- form. The *l*- form, which may be separated from racemic lupanine, has m.p. 43°–44°, and crystallises less easily than the *d*-form. It has been suggested from time to time that lupanine is closely related to sparteine, but according to Beckel (Arch. Pharm. 1911, 249, 329; 1912, 250, 700), this is not the case. All the forms of lupanine are bitter and poisonous (Eichhorn, Nobbes Vers. St. 1867, 272; Siebert, Chem. Soc. Abstr. 1892, 62, 223; Soldaini, Boll. Chem. Farm. 1902, 41, 37; Arch. Pharm. 1902, 240, 260; Davis, Apoth. Zeit. 1896, 11, 94).

Lupinidine. *See Sparteine* (p. 676).

Lupinine $C_{10}H_{19}ON$, an alkaloid found with sparteine (p. 676) in the seeds of *Lupinus luteus* (Linn.) and *L. niger*. Rhombic crystals, m.p. 67°–68°. Distils without decomposition in hydrogen at 255°–257°; lævorotatory. It is bitter and slightly toxic. A tertiary, hydroxy base which furnishes crystalline salts (Baumert, Ber. 1881, 14, 1150; 1882, 15, 1951; Hagen, Annalen, 1885, 230, 370; Siebert, Arch. Pharm. 1891, 229, 531; Soldaini, *ibid.* 1892, 230, 16; Berend, *ibid.* 1897, 235, 262; Willstätter and Fourneau, Ber. 1902, 35, 1910).

Lycoctonine. *See* under *Aconitine* (p. 634).

Mandragorine. *See* under *Atropine and the belladonna alkaloids* (p. 638).

Meteloidine. *See* under *Atropine* (p. 638).

MEZCALINE AND THE ALKALOIDS OF ANHALONIUM SPP.

In Mexico several plants belonging to the genus *Anhalonium*, notably *A. Lewinii* (Hennings), are used in Indian religious ceremonies as narcotics, under the name 'pellote.' The dried flowering heads of *A. Lewinii* are chiefly used for this purpose and come into commerce under the name 'mescal buttons.' From this source and from allied plants a series of alkaloids has been isolated, some of which resemble morphine and others strychnine in their physiological action.

Anhalamine $C_{11}H_{15}O_3N$, microscopic needles, m.p. 185·5°. Occurs in *A. Lewinii* (Hennings). It contains two ·OMe groups and one ·OH group, and is a secondary base (Kander, Arch. Pharm. 1899, 237, 190; Heffter, Ber. 1901, 34, 3004).

Anhaline $C_{10}H_{17}O_3N$, prisms, m.p. 115°, occurs in *A. fissuratum* (Engelm.). Exerts a paralysing action on the central nervous system.

Anhalonidine $C_{12}H_{15}O_3N$, crystalline, m.p. 154°, occurs in *A. Lewinii* (Hennings). Contains one —OH and two —OMe groups, and is a secondary base $OH{\cdot}C_{10}H_7(OMe)_2 : NH$ (Heffter, *ibid.* 1894, 27, 2976).

Anhalonine $C_{12}H_{15}O_3N$, long needles, m.p. 85°, occurs in *A. Lewinii* (Hennings). A secondary base, and contains one —OMe group. It resembles strychnine in its physiological action.

Lophophorine $C_{13}H_{17}O_3N$, syrup, yielding crystalline salts. Occurs in *A. Lewinii* (Hennings). It contains one ·OMe group, and is the most toxic of all the anhalonium alkaloids.

Mezcaline $C_{11}H_{17}O_3N$, colourless, strongly alkaline oil, found in 'mescal buttons' (*Anhalonium Lewinii* [Hennings]), which owe their peculiar properties to its presence. It is a secondary base, contains three ·OMe groups, and on oxidation by permanganate yields 2 : 3 : 4-trimethoxybenzoic acid. Its constitution is still doubtful (Heffter, *l.c.*; and Ber. 1905, 38, 3634).

According to Dixon, anhalonidine, anhalonine, lophophorine, and mezcaline exert qualitatively the same physiological action, lophophorine being the most powerful, and mezcaline the most active in producing colour visions. In man the alkaloids produce first excitement and then intoxication, resembling that caused by alcohol, but accompanied by a number of subjective sensations including colour visions and a feeling of dual existence (J. Physiol. 1899, 25, 69).

Pellotine $C_{13}H_{19}O_3N$, colourless tablets, m.p. 110°; occurs in *A. Williamsii* (Lem.) and also in *A. Lewinii* (Hennings). Possesses slightly narcotic action, and has been employed in medicine as a narcotic.

The chief papers relating to the anhalonium alkaloids, in addition to those already quoted, are Lewin (Arch. expt. Path. Pharm. 1888, 24, 401; 1898, 34, 374; and Heffter, Ber. 1894, 27, 2975; 1896, 29, 216; 1898, 31, 1193).

MORPHINE AND THE OPIUM ALKALOIDS (*see* also *Opium*).

Opium, the partially dried juice of the seed-capsules of *Papaver somniferum* (Linn.), contains the salts (sulphates and meconates) of a large number of alkaloids, of which only the more important will be considered here, viz. morphine $C_{17}H_{19}O_3N$, codeine $C_{18}H_{21}O_3N$ thebaine $C_{19}H_{21}O_3N$, papaverine $C_{20}H_{21}O_4N$, narcotine $C_{22}H_{23}O_7N$, narceine $C_{23}H_{27}O_8N$, and certain secondary alkaloids derived from those named.

The quantity of 'total alkaloids' in opium shows great variation with the geographical source of the drug, but on the average the morphine is about 10 p.c., narcotine 6 p.c., papaverine 1 p.c., codeine 0·5 p.c., and thebaine 0·15 p.c. Indian opium is richer in narcotine and codeine than the Asia Minor (Turkish) opium of commerce.

Morphine Group (*Morphine, Apomorphine, Codeine, Thebaine*).

Morphine $C_{17}H_{19}O_3N$, the first known vegetable alkaloid was isolated from opium about the year 1807 by Sertürner. It is contained in minute amounts in several other plants belonging to the natural order *Papaveraceæ*.

The amount of morphine present in opium varies in the different commercial sorts (Persian, Turkish, Indian, &c.) from 3 to 20 p.c. The British Pharmacopœia specifies that the dried opium intended for medicinal use should contain from 9·5 to 10·5 p.c. of morphine.

Preparation. Morphine exists in opium in the form of two soluble salts (meconate and sulphate), so that extraction with water removes the whole of the alkaloid.

Gregory's method for the manufacture of morphine from opium consists in extracting the drug with lukewarm water, mixing the liquid with excess of chalk, and evaporating to a small volume. Slight excess of calcium chloride is now added, the liquid diluted with water, and the precipitated resin, calcium meconate, &c., filtered off. On concentrating the liquid the hydrochlorides of morphine and codeine crystallise out. These are dissolved in water, the solution decolorised with charcoal and decomposed with excess of ammonia, which precipitates morphine containing a little codeine. For complete separation the codeine may be extracted by one of the solvents, in which it is much more soluble than morphine, *e.g.* ether or benzene.

Properties. Small rhombic prisms or silky needles containing $1H_2O$, which is gradually lost at 100°, more rapidly at 120°. At higher temperatures (about 230°) morphine melts with some decomposition, and afterwards a part of the alkaloid sublimes, together with some of its decomposition products. Slightly soluble in water, 1 in 10,000 at 10°; 1 in 5000 at 20° (Chastaing, Bull. Soc. chim. 1882, [ii.] 37, 477); more soluble in boiling water (1 in 500). Soluble in absolute alcohol (1·1 in 100 at 10°; 8·6 in 100 at b.p.), less so in aqueous alcohol (1 in 100 at 15°; 1 in 36 at b.p.). Less soluble in amyl alcohol (1 in 400 at 11°; 1·1 in 50 at 78°). Very slightly soluble, or nearly insoluble in ether, benzene, chloroform, or light petroleum (Florio, Gazz. chim. ital. 1883, 13, 496; *cf.* Müller, Apoth. Zeit. 1903, 18, 257, and U S. Pharmacopeia, 8th ed.). Readily soluble in solutions of fixed alkalis, especially when warm; less soluble in aqueous ammonia (rel. dens. 0·97) (1 in 177 at 15°). Lævorotatory, in methyl alcohol $[\alpha]_D^{23} = 130{\cdot}9°$. in aqueous soda, $[\alpha]_D = -70{\cdot}23°$; more strongly lævorotatory in neutral or acid solution (Hesse, Annalen, 1875, 176, 190).

Morphine is a strong monacidic base; its alcoholic solution is alkaline to litmus. Dilute acids readily dissolve morphine, and the salts are generally easy to crystallise. The hydrochloride $B{\cdot}HCl,3H_2O$ is a well-crystallised salt, soluble in water (1 in 24 at 15°), less soluble in alcohol (Hesse, *l.c.*). This salt and the sulphate, acetate, and tartrate, &c., are used in medicine. The platinichloride $(B{\cdot}HCl)_2PtCl_4$ is crystalline. The alkaloid and its salts have a bitter taste, and when administered in small doses exert a powerful narcotic action; in larger doses they are poisonous.

Reactions and constitution.

Solution of ferric chloride, almost free from acid, produces with the alkaloid, and with neutral solutions of its salts, a deep-blue coloration, which is discharged by strong acids. This reaction is characteristic and delicate in neutral or nearly neutral solutions. Strong sulphuric acid, free from nitric acid, does not colour morphine unless the mixture is warmed, when a brown coloration is produced. Nitric acid dissolves the alkaloid, with the production of a deep-red colour. If the morphine is first dissolved in strong sulphuric acid and then a drop of nitric acid added, a carmine coloration is observed. Morphine is a powerful reducing agent, converting ferric salts into ferrous salts, solution of potassium ferricyanide into potassium ferrocyanide, and precipitating the metals from solutions of silver nitrate, and gold and platinum chlorides. Since it reduces aqueous iodic acid, liberating iodine, this reaction is often utilised as a test for morphine, the iodine being detected in the usual manner. The salts of morphine also liberate iodine from aqueous iodic acid. Morphine is liable to be mistaken for emetine if colour reactions alone are relied on for its identification (*see* under *Emetine* p. 652, and Allen and Scott-Smith, Analyst, 1902, 27, 345).

Morphine is a tertiary base which combines with 1 mol. prop. of alkyl iodide.

A dibenzoyl and a diacetyl derivative (*heroine*) of morphine have been prepared, whence it may be inferred that the alkaloid contains two hydroxyl groups (Wright, Chem. Soc. Trans. 1874, 27, 1031; Wright and Beckett, *ibid.* 1875, 28, 15; Wright and Rennie, *ibid.* 1880, 37, 610). One of these hydroxyl groups is probably attached to a benzene nucleus, since it has phenolic properties; thus morphine dissolves in alkalis, forming metallic derivatives, in which one atom of hydrogen of the morphine is replaced by metals (Chastaing, Compt. rend. 1882, 94, 44).

When morphine is heated with hydrochloric acid (25 p.c.) in a closed tube at 140°–150°, a molecule of water is separated and *apomorphine* $C_{17}H_{17}O_2N$ is produced. It is isolated by adding sodium bicarbonate in excess to the acid liquid, and shaking with ether, which dissolves the 'apomorphine.' The free base is usually amorphous; it is slightly soluble in cold water, and unstable when exposed to air, absorbing oxygen, especially in presence of alkali, with the production of a green, and afterwards a red, colour. The hydrochloride $B{\cdot}HCl$ is crystalline and is used in medicine. The properties of apomorphine appear to show that the base still contains the phenolic hydroxyl present in morphine. Its physiological action differs entirely from that of morphine, since it produces no narcotic effect, but acts as a powerful emetic (Matthiessen and Wright, Proc. Roy. Soc. 1868–1869, 17, 455; Marmé, Zeitsch. anal. Chem. 1885, 24, 643).

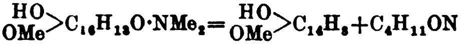
Alkaline solutions of morphine absorb oxygen from the air, which converts the morphine into *pseudomorphine* (oxydimorphine) $C_{34}H_{36}O_6N_2$, a base which also results from the action of weak oxidising agents on morphine, and is found in small quantity in opium (Hesse, Annalen, 1867, 141, 87; 1875, 175, 195; 1884, 222, 234; 1886, 234, 255). It is not poisonous.

The reactions, which are of primary importance as regards the constitution of morphine, and the closely related alkaloids, codeine and thebaine, are as follows—

1. Of the three oxygen atoms in morphine one is phenolic, and on methylation gives rise to codeine; the second is alcoholic; the third oxygen atom is non-reactive, and is present in a heterocyclic nucleus.
2. The nitrogen atom is tertiary.
3. On distillation with zinc dust morphine yields phenanthrene.
4. With methyl iodide morphine furnishes codeine methiodide; this on warming with silver hydroxide gives codeine methylhydroxide $MeO(HO){\cdot}C_{16}H_{14}O{\cdot}NMe_2OH$, which immediately decomposes, giving methylmorphimethine

$$MeO(OH){\cdot}C_{16}H_{12}O{\cdot}NMe_2$$

by loss of H_2O. This base when heated with hydrochloric acid or acetic anhydride is decomposed in part, forming methylmorphol and hydroxyethyldimethylamine—



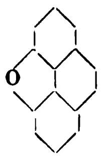
$$\left.\begin{matrix}HO\\OMe\end{matrix}\right>C_{16}H_{12}O{\cdot}NMe_2=\left.\begin{matrix}HO\\OMe\end{matrix}\right>C_{14}H_8+C_4H_{11}ON$$

Methylmorphimethine. Methylmorphol Hydroxyethyldimethylamine.

Methylmorphol is known to be 4-hydroxy-3-methoxyphenanthrene (Pschorr and Sumuleanu, Ber. 1900, 33, 1810). Hydroxyethyldimethylamine probably results from the addition of water to vinyldimethylamine first liberated thus

$$NMe_2{\cdot}CH:CH_2 \rightarrow NMe_2{\cdot}CH_2{\cdot}CH_2OH$$

It follows from the above that morphine must be built up from the complexes



and $—CH_2{\cdot}CH_2{\cdot}NMe—$

The two complexes have been 'assembled' in various ways, but Pschorr's formula is that now generally accepted (*see* p. 659 under *Thebaine*).

Detection. Morphine affords precipitates with most of the alkaloidal reagents. It may be identified by means of the properties and reactions described above. The characteristic reactions of morphine can, however, only be relied on when a nearly pure alkaloid has been experimented with. Unfortunately, morphine is one of the most difficult alkaloids to separate from much organic impurity, especially when it is present only in minute quantity, as is generally the case in toxicology. Since the internal administration of opium, and not of morphine itself, is often the cause of poisoning, the existence of this alkaloid may be confirmed by detecting meconic acid, which is easy to recognise.

For a detailed account of the qualitative reactions of morphine, *see* Marmé, *l.c.*

Estimation. The following method may be adopted for the estimation of morphine in opium: 14 grms. of powdered opium dried at 100° are mixed with 6 grms. of slaked lime, and stirred in a mortar with 40 c.c. of water. The mixture is diluted with 100 c.c. of water and occasionally stirred during about half an hour. The mixture is then filtered into a stoppered bottle, until a volume of 104 c.c., representing 10 grms. of opium, has been obtained. To this filtrate 10 c.c. of 90 p.c. alcohol are added and 50 c.c. of ether and the mixture shaken. In order to precipitate the morphine from its solution in the lime-water, 4 grms. of ammonium chloride are added and the mixture well shaken. After the lapse of 12 hours the morphine will have crystallised out. Decant the ethereal layer and filter it through a small counterbalanced paper. Add 20 c.c. of ether to the contents of the bottle, shake gently, again decant and filter the ethereal layer. Wash the filter paper with 10 c.c. of ether and dry it. Now filter off the crystals which remain in the bottle, using a saturated solution of morphine in water for washing. The crystals of morphine are dried first at 55°–60°, and then at 110° for two hours and weighed. 0·5 grm. of the crystals obtained is then titrated with N/10 sulphuric acid, using litmus paper as indicator. The weight of morphine as determined by titration +0·014 grm. (correction for loss) should be 0·95 to 1·05 grm.

For an account of the different methods which have been proposed, *v.* Allen's Organic Analysis, 4th ed. vol. vi.

For the estimation of morphine in tincture of opium (laudanum) the following method may be employed: 80 c.c. of the laudanum are evaporated to 30 c.c. on the water-bath, and the residue thoroughly mixed with 3 grms. of calcium hydroxide, and diluted to 85 c.c. with water. The liquid is then filtered, and 50 c.c. of the filtrate (representing the same quantity of laudanum) are mixed with 5 c.c. of alcohol (90 p.c.), 30 c.c. of ether, and 2 grms. of ammonium chloride. The mixture is well shaken and allowed to remain for 12 hours. The crystals of morphine, which will have separated, are collected, with the precautions described above for the estimation of morphine in opium, 15 c.c. of ether being used to rinse the contents of the bottle and 10 c.c. to wash the filter paper. For titrations 0·3 grm. of the crystals used and to the weight determined by titration 0·1 grm. per 100 c.c. of filtrate used are added as a correction for loss. 100 c.c. of the tincture should yield not less than 0·7 nor more than 0·8 grm. of anhydrous morphine.

Codeine (*Methylmorphine*) $C_{18}H_{21}O_3N$ exists in small quantity in opium.

Preparation. The mixed hydrochlorides of morphine and codeine, having been separated from opium by Gregory's method (*see preparation of morphine*), and the morphine precipitated by ammonia, the alkaline filtrate, which contains codeine hydrochloride, is evaporated to a small volume and precipitated by potash. The codeine is purified by crystallisation from ether or from water. Codeine may be prepared from morphine by heating it with alcoholic soda and methyl iodide (Grimaux, Ann. Chim. Phys. 1882, [v.] 27, 273; Hesse, Annalen, 1884, 222, 210), or by the action of potassium methyl sulphate on morphine dissolved in methyl alcohol.

Properties. Large rhombic crystals from water with $1H_2O$, which melt in boiling water; small anhydrous crystals from ether, m.p. 155°. Lævorotatory $[\alpha]_D - 137{\cdot}75°$ in alcohol. Slightly soluble in cold water, more soluble in hot water, alcohol, ether, or benzene; sparingly soluble in light petroleum. The aqueous solution is strongly alkaline. Codeine is a monacidic base; the principal salts are crystalline and soluble in water. In physiological action codeine and its salts resemble morphine, but are less poisonous.

Reactions and constitution. Codeine is distinguished from morphine by not giving the colour reaction with ferric chloride, and by producing with nitric acid a yellow, and not a red, colour. Concentrated sulphuric acid does not colour codeine except after prolonged standing, but if a trace of nitric acid or ferric salt is added to the mixture it becomes blue. For an account of the qualitative reactions of codeine, *see* Marmé, Zeitsch. anal. Chem. 1885, 24, 643. The decomposition products of codeine are, for the most part, analogous to those of morphine (p. 657), of which it is the methyl derivative. The methyl group replaces an atom of hydrogen in the phenolic hydroxyl group of morphine (for formula, *see* p. 659).

Estimation. The following process has been devised by Andrews (Analyst, 1911, 36, 489). Dry opium (12 grms.) is exhausted by successive portions of cold water, the filtrate made up to 100 c.c., and 20 c.c. of 20 p.c. lead acetate solution added, to remove colouring matter and some narcotine. The mixture is kept overnight, then passed through a filter paper in a Buchner funnel, and from 100 c.c. of the filtrate (10 grms. of opium) the excess of lead is removed by hydrogen sulphide, and this in turn removed by a current of air. The washings from the lead sulphide precipitate are collected separately, evaporated to a small bulk, and added to the main filtrate, which should then not exceed 130 c.c. To this 20 c.c. of a 20 p.c. solution of sodium salicylate are added, and the flask containing the mixture corked and shaken. A resinous precipitate separates leaving a nearly clear liquor, which is passed through a small pleated filter, into a beaker containing a few crystals of thebaine salicylate, to facilitate the separation of this salt from the filtrate, which is well stirred to assist this operation. After standing over-night the liquid is again passed through the same pleated filter and the treatment repeated until no further deposition of solid matter takes place. The final filtrate and washings, concentrated to about 10–15 c.c. on a water-bath, are transferred while still warm to a glass separator (No. 1), the washings of the dish being placed in a second separator (No. 2). The contents of No. 1 are washed with three successive portions of ether, each portion being in turn also used to wash the contents of No. 2. The latter are finally added to separator No. 1, and 10 c.c. of a 20 p.c. solution of caustic soda added, to keep the morphine dissolved. This strongly alkaline liquid is extracted four times succession with rather more than its own volume of ether, each portion of ether, as separated, being washed with 20–30 c.c. of water and finally run into a dry flask containing anhydrous sodium sulphate to dry it. The dry ethereal solution of codeine is distilled in a flask down to a few c.c., which are allowed to evaporate spontaneously, when, as a rule, the codeine separates in well-defined crystals, and after drying can be weighed, the weight being checked by dissolving in excess of N/10 acid and titrating back with N/10 sodium hydroxide, using litmus or methyl-orange as indicator.

Thebaine $C_{19}H_{21}O_3N$ occurs in small quantity (up to 1 p.c.) in opium, and remains in the mother liquor after the separation of morphine and codeine hydrochlorides (p. 656). It is precipitated from this along with narcotine and papaverine by addition of ammonia. The precipitate is dried and dissolved in boiling alcohol. On cooling narcotine and papaverine crystallise out. The filtrate is evaporated to dryness, the residue dissolved in acetic acid, and the solution decolorised with lead acetate. From the filtrate, after removal of excess of lead by hydrogen sulphide, thebaine is precipitated by adding ammonia.

Properties and reactions. Leafy or prismatic crystals, m.p. 193°. Lævorotatory. Nearly insoluble in cold water, slightly soluble in ether, very soluble in alcohol, chloroform, or benzene. Slightly soluble in aqueous alkalis. Thebaine is a monacidic base; the principal salts are crystalline and soluble in water. The alkaloid and its salts are poisonous and exercise a tetanising action, but are less powerful than strychnine and its salts. Thebaine is coloured bright red by concentrated sulphuric acid. It is converted into thebenine when warmed with dilute acids, and is attacked by concentrated hydrochloric acid, with the formation of morphothebaine, isomeric with thebenine $C_{18}H_{19}O_3N$.

CONSTITUTION. Thebaine is related somewhat closely to morphine and its methyl ether, codeine, as inspection of slightly extended formulæ for the three alkaloids shows—

$$\left.\begin{matrix}\mathrm{HO}\\\mathrm{HO}\end{matrix}\right>C_{16}H_{14}O\cdot NMe \qquad \left.\begin{matrix}\mathrm{MeO}\\\mathrm{HO}\end{matrix}\right>C_{16}H_{14}O\cdot NMe$$

Morphine. Codeine.

$$\left.\begin{matrix}\mathrm{MeO}\\\mathrm{MeO}\end{matrix}\right>C_{16}H_{12}O\cdot NMe$$

Thebaine.

When codeine is oxidised by chromic acid the alcoholic hydroxyl group is converted into a carbonyl group with the formation of codeinone, thus—

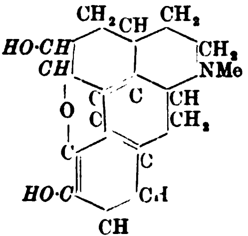
$$\left.\begin{matrix}\mathrm{MeO}\\\mathrm{HO}\end{matrix}\right>C_{16}H_{14}O\cdot NMe \rightarrow \left.\begin{matrix}\mathrm{MeO}\\\mathrm{O}\end{matrix}\right>C_{16}H_{13}O\cdot NMe$$

Codeine. Codeinone.

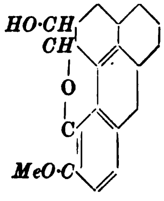
On treatment with dilute acids both thebaine (Howard and Roser, Ber. 1886, 19, 1596; and Freund, *ibid.* 1899, 32, 168) and codeinone (Knorr, *ibid.* 1903, 36, 3074) yield thebenine, whilst with strong acids they furnish the isomeric morphothebaine (*l.c.*). Further, hot acetic anhydride decomposes thebaine (Freund, *ibid.* 1897, 30, 1357) and codeinone (Knorr, *l.c.*) in the following ways (*cf.* Pschorr, Seydel and Stöhrer, *ibid.* 1902, 35, 4400)—

Codeinone → 6-Methoxy-3 : 4-dihydroxyphenanthrene }
Thebaine → 3 : 6 - Dimethoxy - 4-hydroxyphenanthrene } + hydroxyethylmethylamine

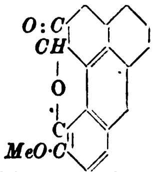
Thebaine must therefore be the methyl ether of an enolic form of codeinone. Accepting Pschorr's formulation of morphine, the three alkaloids, codeine, codeinone, and thebaine, will be represented by the following formulæ in which the variable groups only are shown in the last three (Ber. 1902, 35, 4382; 1905, 38, 3160; 1907, 40, 1984; *cf.* Knorr and others, *ibid.* 1907, 40, 3341, 4891, Wieland and Kappelmeier, Ann. 1911, 382, 306; Freund. Ber. 1905, 38, 3238; 1910, 43, 2128).



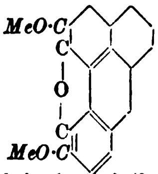
Morphine (Pschorr).



Codeine.



Codeinone (keto form).



Thebaine (methyl ether of *enol*codeinone).

Narcotine Group (Narcotine, Gnoscopine, Hydrocotarnine, Narceine).

Narcotine $C_{22}H_{23}O_7N$ usually occurs to the extent of about 5–6 p.c. in Asia Minor opium, but in larger quantity in Indian and Persian opiums. Unlike most alkaloids, narcotine appears, as a rule, to exist in the plant in the free state, and not as a salt.

Preparation. If the opium is extracted with water in order to isolate the morphine, &c., the greater part of the narcotine remains undissolved, since this alkaloid is nearly insoluble in water. By exhausting the residue with dilute hydrochloric acid, the narcotine is removed as hydrochloride, and from the solution of this salt the base may be precipitated by sodium bicarbonate, and crystallised from alcohol. Or the narcotine may be extracted from the opium by boiling it with ether; *see* also Hesse, Annalen, Suppl. 8, 284.

Estimation. Narcotine is most readily estimated in opium by drying the drug at 100° and then extracting a weighed quantity with hot ether. From the ether solution the alkaloid may be extracted by repeated agitation with dilute sulphuric acid, and may be obtained clean by adding alkali and re-extracting with ether.

Properties. Prismatic crystals, m.p. 174°–175°. Almost insoluble in water (1 in 25,000 at 15°, 1·1 in 7000 at 100°); soluble in alcohol (1 in 100 at 15°, 1 in 20 at b.p.); ether (1 in 166 at 16°); and in benzene (1 in 22 at 15°); very soluble in chloroform (1 in 2·69 at 15°); slightly soluble in amyl alcohol or light petroleum, dissolves in lime or baryta water, and slightly in aqueous ammonia. Lævorotatory, $[a]_D = -185°$ in alcohol (Hesse, Annalen, 1875, 176, 192), $-199·9°$ in chloroform (Perkin and Robinson, Chem. Soc. Proc. 1910, 26, 131). The solution in dilute acids is dextrorotatory. Narcotine is a feeble monacidic tertiary base; its aqueous solution is neutral to litmus. The principal salts crystallise with difficulty; their aqueous solutions are acid, and are decomposed, with separation of narcotine when evaporated. The free alkaloid may even be extracted from the aqueous solution of some narcotine salts by agitating with ether or chloroform. In larger doses than are necessary in the cases of morphine and codeine, narcotine and its salts exert a narcotic action.

Reactions and constitution. Concentrated sulphuric acid dissolves narcotine, and the solution soon becomes yellow; on warming a rapid transition of different colours is observed, the mixture becoming orange-red, blue, and finally purple. Nitric acid dissolves the alkaloid with a yellow colour.

When heated with hydriodic acid narcotine furnishes three molecular proportions of methyl iodide and *nornarcotine* $C_{19}H_{17}O_7N$ or

$$C_{19}H_{14}(OH)_3O_4N.$$

The less energetic action of hydriodic acid produces one molecular proportion of methyl iodide, and *dimethylnornarcotine*

$$C_{19}H_{14}(OCH_3)_2(OH)O_4N,$$

or two molecular proportions of methyl iodide and *methylnornarcotine* $C_{19}H_{14}(OCH_3)(OH)_2O_4N$.

When heated with water in a closed tube at 100°, or by prolonged ebullition with water, the alkaloid is resolved into *opianic acid*

$$C_6H_2(OMe : OMe : COOH : CHO = 1 : 2 : 3 : 4)$$

and *hydrocotarnine*

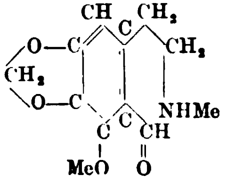
$$(C_{22}H_{23}O_7N + H_2O = C_{10}H_{10}O_5 + C_{12}H_{15}O_3N)$$

from which cotarnine $C_{12}H_{15}O_4N$ results by oxidation (Beckett and Wright, Chem. Soc. Trans. 1875, 28, 583). Cotarnine is largely employed in the form of its chloride (stypticin) as an internal styptic (*cf. Hydrastinine*, p. 654).

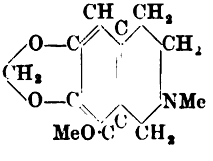
Nascent hydrogen converts narcotine into *meconin* and *hydrocotarnine* $C_{12}H_{15}O_3N$, and on oxidation *cotarnine* and *opianic acid* (*see* above) are formed, the latter by further oxidation becoming *hemipinic acid*.

$$C_6H_2(OMe : OMe : COOH : COOH = 1 : 2 : 3 : 4).$$

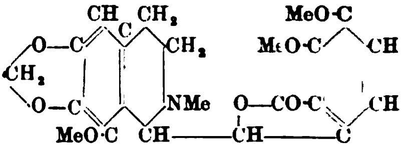
On 'exhaustive methylation' cotarnine yields *cotarnone* $C_{11}H_{10}O_4$, which on oxidation gives *cotarnic acid* $C_{10}H_8O_7$, and this with hydrochloric acid furnishes the methylmethylene ether of gallic acid. From these and other data Roser has assigned the following formulæ to cotarnine, hydrocotarnine, and narcotine (Annalen, 1888, 249, 156, 168; 1889, 254, 334, 351; 1893, 272, 221; *cf.* Freund and Becker, Ber. 1903, 36, 1521)—



Cotarnine.



Hydrocotarnine.



Narcotine.

The synthesis of narcotine has been effected by Perkin and Robinson by treating an alcoholic solution of cotarnine and meconin with potassium carbonate, or by simply boiling an alcoholic solution of these two substances (Chem. Soc. Proc. 1910, 26, 46; Chem. Soc. Trans. 1911, 99, 778; *cf.* Liebermann, Ber. 1896, 29, 184). Cotarnine had been prepared previously by Salway (Chem. Soc. Trans. 1910, 97, 1208) from myristicin. The substance actually produced in Perkin and Robinson's synthesis is the alkaloid *gnoscopine*, isolated from opium by T. and H. Smith (Pharm. J. 1878, [iii.] 9, 82; 1893, [iii.] 52, 794), and which Rabe had suggested (Ber. 1907, 40, 3280; 1910, 43, 800; Annalen. 1910, 377, 223) was *dl*-narcotine produced by racemisation of narcotine during its isolation from opium. Natural and synthetic gnoscopines were resolved by crystallising the *d*-camphorsulphonate into *d*- and *l*-narcotine, the latter identical with the natural alkaloid, by Perkin and Robinson (Chem. Soc. Proc. 1910, 26, 46, 131).

Narceine $C_{23}H_{27}O_8N,H_2O$ occurs in opium to the extent of 0·1 p.c., and is recovered from the mother liquors from which morphine and codeine hydrochlorides have crystallised out, after the removal from these of narcotine, thebaine, and papaverine (pp. 656, 659).

Properties. Crystallises from water or alcohol in prisms or slender needles with $3H_2O$, m.p. 170°, or 140°–145° ($1H_2O$) when dried at 100°. Sparingly soluble in cold water (1 in 1285 at 13°) or cold alcohol (1 in 945 of 80 p.c. alcohol), much more soluble in hot water or hot alcohol. Somewhat soluble in ammonia and alkalis. Optically inactive. Narceine has no marked physiological action. It is a monacidic base and forms well-crystallised salts with acids. It also behaves as a monocarboxylic acid and forms a series of salts with metals (potassium-narceine

$$C_{23}H_{26}O_8NK,$$

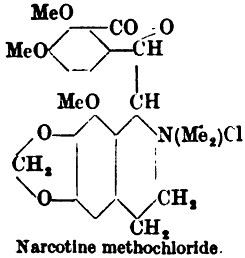
rosettes of needles), and yields esters with alcohols (narceine ethyl ester hydrochloride

$$C_{23}H_{26}(C_2H_5)O_8N,HCl$$

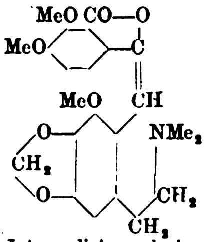
is crystalline, m.p. 206°–207°). Methyl iodide reacts with narceine to form narceine methyl ester methiodide $C_{23}H_{26}(CH_3)O_8N,CH_3I$, m.p. 193°–194°.

Reactions and constitution. Narceine gives with chlorine water, followed by ammonia solution, a blood-red coloration. Its constitution is established by the fact that it can be prepared by heating narcotinemethochloride with alkalis. According to Freund this change takes place as shown by the formulæ at top of next page.

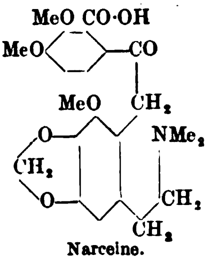
The chief papers relating to narceine are Pelletier, Annalen, 1832, 5, 163; Anderson, *ibid.* 1853, 86, 182; Hesse, *ibid.* 1875, 176, 189; Roser, *ibid.* 1888, 247, 169; Freund and collaborators, *ibid.* 1893, 277, 6; Ber. 1909, 42, 1084).



Narcotine methochloride.



Intermediate product.



Narceine.

Papaverine Group (*Papaverine*, *Laudanosine*, *Laudanine*, &c.).

Papaverine $C_{20}H_{21}O_4N$. This alkaloid separates with narcotine as described under thebaine (p. 659) and is separated from it by conversion into the acid oxalate, which is sparingly soluble in alcohol, that of narcotine being readily soluble.

Properties. Prismatic crystals, m.p. 147°. Very slightly soluble in hot or cold water; easily soluble in hot alcohol, chloroform, or benzene. Optically inactive. A monacidic base which forms crystalline salts. It is mildly soporific in action.

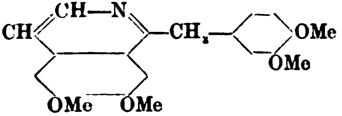
Reactions and constitution. Sulphuric acid dissolves papaverine in the cold without coloration. Commercial papaverine gives a violet coloration due to the presence of cryptopine (p. 650) (Pictet and Kramers, Ber. 1910, 43, 1329). With sulphuric and iodic acids it gives a purple coloration changing to green.

Nascent hydrogen converts papaverine into a dihydride (Pyman, Chem. Soc. Trans. 1909, 95, 1610). When heated with concentrated hydriodic acid it furnishes papaveroline $C_{16}H_{13}O_4N$, together with four molecular proportions of methyl iodide, from which it is inferred that four methoxyl groups are present.

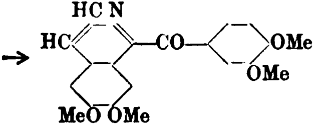
On oxidation with permanganate papaverine yields a large number of products, the principal being *veratric acid*, *metahemipinic* or *dimethoxy*-o-*phthalic acid* $C_6H_2(OCH_3)_2(CO_2H)_2$, *pyridine-αβγ-tricarboxylic acid*, and *papaveraldine*. According to Dobson and Perkin (Chem. Soc. Trans. 1911, 99, 135) papaveraldine (*see* below) is identical with *xanthaline*, an alkaloid isolated from opium by T. and H. Smith (Pharm. J. 1893, [iii.] 52, 793).

When fused with alkali papaverine affords *veratric acid*, together with *dimethoxy*-iso-*quinoline*.

From these and other results Goldschmiedt (Monatsh. 1883, 4, 704; 1885, 6, 372, 667, 956; 1886, 7, 488; 1887, 8, 510; 1888, 9, 42, 327, 349) has concluded that papaverine is tetramethoxybenzyl*iso*quinoline, and this constitution has been established by synthesis of the alkaloid (Pictet and Gams, Compt. rend. 1909, 149, 210).

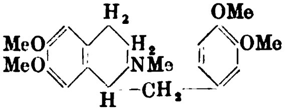


Papaverine.



Papaveraldine (xanthaline).

Laudanosine, $C_{21}H_{27}O_4N$. When papaverine methochloride is reduced with tin and hydrochloric acid it furnishes *dl-N*-methyltetrahydropapaverine, m.p. 115°, and this on crystallisation of the quinate, separates into the *d*- and *l*-bases, the former being identical with d-*laudanosine* which occurs in opium. It crystallises in needles, m.p. 89°, $[\alpha]_D + 103°$ in alcohol and contains four ·OMe groups. Laudanosine is more poisonous than papaverine, and resembles thebaine in physiological action; it exerts no narcotic effect (Pictet and Athanasescu, Ber. 1900, 33, 2346). *dl*-Laudanosine is also formed when *laudanine* $C_{20}H_{25}O_4N$, crystals, m.p. 166°, $[\alpha]_D = 0°$, an alkaloid occurring in opium, is methylated, so that it appears to be the methyl ether of laudanine (Hesse, Annalen, 1894, 282, 208; J. pr. Chem. 1902, [ii.] 65, 42). Syntheses of laudanosine have been effected by Pictet and Mdlle. Finkelstein (Compt. rend. 1909, 148, 925), and by Gadamer (Arch. Pharm. 1911, 249, 680; *cf.* Pschorr, Ber. 1904, 37, 1926), so that the constitution of the alkaloid is now clearly established—



Laudanosine.

Laudanine differs from laudanosine only in containing a hydroxyl group in place of a methoxyl (probably in the benzene ring). The alkaloid *laudanidine*, isomeric with laudanine, which also occurs in opium, is probably *l*-laudanine. It resembles laudanine in crystalline form and in its reactions, but melts at 177° and has $[\alpha]_D - 87{\cdot}8°$ in chloroform (Hesse, Annalen, 1894, 282, 208).

Muscarine $C_5H_{15}O_3N$ occurs in various poisonous fungi, especially in fly agaric (*Amanita muscaria*). Hygroscopic crystals. Tasteless. Its constitution is uncertain, but it is believed to be the hydrated aldehyde of choline (Berlinerblau, Ber. 1884, 17, 1139; E. Fischer, *ibid.* 1893, 26, 468; 1894, 27, 165; Nothnagel, *ibid.* 1893, 26, 801). Choline on oxidation furnishes a muscarine, which is not identical in physiological actions with the natural one. Muscarine somewhat resembles pilocarpine in physiological action, is antagonistic to atropine and highly toxic (*v.* PTOMAINES).

Myoctonine. *See* under *Aconitine and the aconite alkaloids* (p. 634).

Napelline. A name applied by Hubschmann to what was probably a mixture of amorphous alkaloids from *Aconitum Napellus* (Linn.). *See Aconite and the aconite alkaloids* (p. 630).

Narceine. *See* under *Morphine* (p. 660).

Narcissine $C_{16}H_{17}O_4N$, occurs in the bulbs of *Narcissus Pseudo-Narcissus* (Linn.) and *Buphane disticha*; crystals, m.p. 266°–267° $[a]_D^{10}$—95·8° in alcohol. Causes nausea and purgation (Ewins, Chem. Soc. Trans. 1910, 97, 2406; Tutin, *ibid.* 1911, 99, 1240).

Narcotine. *See* under *Morphine* (p. 659).

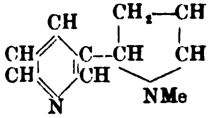
Nicotine $C_{10}H_{14}N_2$, a liquid, volatile alkaloid, occurring in tobacco (*Nicotiana Tabacum* [Linn.]) as malate and citrate, together with several other alkaloids of comparatively little importance, *e.g.* *nicoteine* $C_{10}H_{12}N_2$, b.p. 266°, liquid; *nicotimine* $C_{10}H_{14}N_2$, b.p. 250°–255°, liquid; *nicotelline* $C_{10}H_8N_2$, m.p. 148°, prismatic needles. Nicotine also occurs in *Duboisia Hopwoodii* (F. Muell.) (Rothera, Bio-Chem. J. 1910, 5, 193), from which it was isolated under the name 'piturine' (*see* Petit, Pharm. J. 1878–1879, [iii.] 9, 819). Tobacco contains, as a rule, from 1 to 8 p.c. of nicotine, but by far the greater proportion of commercial tobacco contains not more than 4 p.c. (*v.* TOBACCO).

Preparation. Nicotine and tobacco extract are now largely used as insecticides, and a considerable industry has sprung up in the last few years in the manufacture of these products. For these purposes tobacco leaf midribs and waste tobacco are largely used, as well as the liquors obtained in the manufacture of chewing tobacco. The tobacco is extracted with water usually in some form of continuous extraction apparatus, and this liquor, or that produced in making chewing tobacco, is concentrated to form tobacco extract. From the latter crude nicotine can be obtained by adding lime or soda solution and steam-distilling, the distillate being extracted with ether.

Estimation. The process generally employed for this purpose is that of Kissling (Zeitsch. anal. Chem. 1882, 21, 64; 1883, 22, 199), which has been modified in various ways. The following form of this process is stated to give good results: 20 grms. of powdered tobacco, dried at a temperature not exceeding 60°, is mixed with 10 c.c. of alcohol containing 0·6 grm. of sodium hydroxide and extracted with ether in a Soxhlet apparatus until exhausted (usually in 3 hours). The solvent is distilled off and the residue mixed with 50 c.c. of 0·4 p.c. soda solution and steam-distilled, and the distillate titrated with N-sulphuric acid in presence of rosolic acid. For extracts the same process may be used, alkali being added to the extract and the mixture steam-distilled. For recent work on the estimation of nicotine in tobacco and tobacco extracts, *see* Tóth, Rev. Intern. Fals. 1901, 14, 12; Chem. Zeit. 1911, 35, 146, 926; Bertrand and Javillier, Bull. Soc. chim. 1909, [iv.] 5, 241; Ann. Chim. anal. 1911, 16, 251; Schröder, Chem. Zeit. 1911, 35, 30, 382; *cf.* Kissling, *ibid.* 98, 200, and Leister, *ibid.* 239; Koenig, *ibid.* 1911, 35, 521; Surre, Ann. Falsif. 1911, 4, 331 (a process for estimating nicotine in presence of pyridine bases).

Properties. Pungent, colourless, hygroscopic liquid, which oxidises in air becoming brown and resinous, b.p. 247°. Distils unchanged in a current of hydrogen or steam, but suffers oxidation when distilled in air, sp.gr. 1·0110 at 20°. The density increases to 1·04 on addition of water up to 33 p.c. (*cf.* Hudson, Zeitsch. physikal. Chem. 1904, 47, 113). Lævorotatory $[a]_D = -163·85°$; salts dextrorotatory. The aqueous solution is strongly alkaline and precipitates solutions of many metallic salts. The salts crystallise with difficulty, but the picrate $B,2C_6H_2(NO_2)_3OH$ forms glancing yellow prisms, m.p. 218°, and is characteristic. Nicotine and its salts are precipitated even in dilute solutions by alkaloidal reagents. Nicotine treated with a drop of formaldehyde solution and then with a drop of nitric acid gives a rose-red coloration.

Reactions and constitution. Nicotine reacts with methyl iodide as a ditertiary base, and on oxidation furnishes β-pyridine derivatives, so that it must contain a pyridine nucleus, with a side chain or a second ring attached in the β-position. Pinner first suggested that this residual portion of the molecule consisted of a N-methylpyrrolidine ring (Ber. 1892, 25, 2816; 1893, 26, 292, 769), and this has received support from the synthesis of nicotine by Pictet and collaborators (*ibid.* 1895, 28, 1911; 1898, 31, 2018; 1900, 33, 2355; 1904, 37, 1225).



Nicotine (Pinner).

Oxyacanthine. *See* under *Berberine* (p. 640).

Palmatine. *See* under *Columbamine* (p. 648).

Palmatisine. *See* under *Aconitine* (p. 634).

Papaverine. *See* under *Morphine and the opium alkaloids* (p. 661).

Paucine $C_{27}H_{39}O_5N_5$, obtained from the seeds of *Pentaclethra macrophylla* (Benth.) sometimes imported from West Africa as an oil-seed ('Owala beans'). Yellowish leaflets with $6\frac{1}{2}H_2O$, m.p. 126°. Salts crystalline. Poisonous (Merck's Bericht, 1894, p. 11).

PELLETIERINE AND THE ALKALOIDS OF POMEGRANATE ROOT BARK.

Tanret isolated from the bark four alkaloids (Compt. rend. 1878, 86, 1270; 1879, 88, 716; 1880, 90, 696), to which a fifth, *iso*methylpelletierine was added by Piccinini (Gazz. chim. ital. 1899, 29, 311). The alkaloids known to occur in the bark are—

Pelletierine $C_8H_{15}ON$
*iso*Pelletierine $C_8H_{15}ON$
Methylpelletierine $C_9H_{17}ON$
*iso*Methylpelletierine $C_9H_{17}ON$
*pseudo*Pelletierine $C_9H_{15}ON$.

The bark has long been used as an anthelmintic, and Schroeder has observed that the first two alkaloids in the above list have a specific action on tape worms. None of the alkaloids are very active poisons, though in large doses the first two produce toxic effects.

Preparation (*see* Tanret, *l.c.*).

Estimation (*see* Ewers, Arch. Pharm. 1899, 237, 49, and German Pharmacopeia v.). According to Ewers (*l.c.*) pomegranate root bark contains 0·63–0·72 p.c. total alkaloids, of which 40–50 p.c. consists of the active alkaloids pelletierine and *iso*pelletierine; branch bark contains 0·52 p.c. total alkaloids. The quantity of alkaloids diminishes on long storage of the bark.

Pelletierine $C_8H_{15}ON$. Liquid, sp.gr. 0·9 at 0°. Darkens and resinifies in air, by

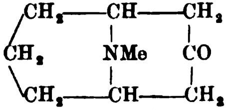
195°. Dextrorotatory $[\alpha]_D = +8°$. Soluble in water (1 in 23 at 15°); readily soluble in alcohol, ether, or chloroform. The aqueous solution is strongly alkaline. The salts are crystalline; the sulphate is lævorotatory.

***iso*Pelletierine** $C_8H_{15}ON$ closely resembles pelletierine, but is optically inactive.

Methylpelletierine $C_9H_{17}ON$, liquid, b.p. 215°; the hydrochloride is dextrorotatory and hygroscopic (Tanret, *l.c.*; and Bull. Soc. chim. 1879, [ii.] 32, 464, 466; 1881, [ii.] 36, 256).

***iso*Methylpelletierine** $C_9H_{17}ON$, liquid, b.p. 114°–117°/26 mm., strongly alkaline; the aurichloride, m.p. 115°–117°, forms orange-yellow rosettes. The alkaloid contains a : NMe and a : CO group (Piccinini, *l.c.*).

***pseudo*Pelletierine** $C_9H_{15}ON$ forms prismatic crystals from light petroleum, m.p. 48°, b.p. 246°. Easily soluble in ether, chloroform, or alcohol. Strong, optically inactive base, forming crystalline salts. The oxygen atom is present as carbonyl. Ciamician and Silber have shown (Ber. 1892, 25, 1601; 1893, 26, 156, 2740; 1894, 27, 2851; 1896, 29, 492) that *pseudo*pelletierine yields a series of derivatives which bring it into close relationship with tropine (p. 637). Piccinini has extended these observations (Gazz. chim. ital. 1899, 29, i. 408; ii. 115; 1901, 31, i. 561), and using Willstätter's formula for tropine (p. 637) as a basis, has assigned the following constitution to *pseudo*pelletierine (*cf.* Willstätter and Veraguth, Ber. 1905, 38, 1984)—



*pseudo*Pelletierine.

Pellotine. *See* under *Mezcaline* (p. 656).
Pelosine. *See Bebeerine* (p. 639).

Physostigmine and the Alkaloids of Calabar Bean.

Physostigmine (*Eserine*) $C_{15}H_{21}O_2N_3$, the chief alkaloid of Calabar bean (*Physostigma venenosum* [Balf.]). (*v.* Ordeal Bean, vol. iv. p. 21).

Preparation. The powdered beans are extracted with alcohol and the alcohol distilled off. The extract is mixed with excess of sodium carbonate and extracted repeatedly with ether; the ethereal solution is shaken with successive portions of dilute sulphuric acid (5 p.c.) until the aqueous liquid extract becomes just acid. It is then filtered and the physostigmine precipitated as salicylate. From the mother liquor a further portion may be obtained by repetition of the treatment. From the salicylate the alkaloid may be recovered by agitation with aqueous sodium carbonate in presence of ether and re-crystallising from benzene and light petroleum (Jobst and Hesse, Annalen, 1864, 129, 115; Vée, J. 1865, 456; Hesse, Annalen, 1867, 141, 82; Petit and Polonowsky, Bull. Soc. chim. 1893, [iii.] 9, 1008; Orloff, Chem. Zeit. 1897, 1214; Salway, Chem. Soc. Trans. 1911, 99, 2148).

Estimation of physostigmine. 20 grams of Calabar beans in No. 60 powder are macerated with 200 c.c. of ether and 10 c.c. of 10 p.c. sodium carbonate solution during 4 hours. 100 c.c. of ether are withdrawn and the alkaloids extracted by shaking with several portions of N/10 acid. The combined acid liquids are made alkaline with 10 p.c. sodium carbonate solution, and the alkaloid extracted by shaking at least ten times with ether using 20 c.c. ether each time. The combined ethereal solutions are shaken once with 5 c.c. of water, and the residue left on distilling off the solvent, dissolved in 5 c.c. N/10 acid, and titrated back with N/50 alkali, using iodo-eosin as indicator (Salway, Amer. J. Pharm. 1912, 84, 49).

Properties. The alkaloid is dimorphous and forms stout prisms, m.p. 86°–87°, or 105°–106°; lævorotatory $[\alpha]_D -75{\cdot}8°$ in chloroform (Salway, *l.c.*). Very slightly soluble in water, but readily soluble in alcohol, ether, chloroform, or benzene. Strongly alkaline. The sulphate $B_2{\cdot}H_2SO_4{,}xH_2O$, colourless needles, m.p. 140°, is very soluble in water, alcohol, or chloroform, less so in ether (1 in 200 at 25°); the salicylate $B{\cdot}C_7H_6O_3$ forms acicular crystals, m.p. 180–181°, and is soluble in water (1 in 72·5 at 25°), alcohol (1 in 12·7 at 25°), ether (1 in 175 at 25°), or chloroform (1 in 8·6 at 25°). Both these salts are used in medicine. The alkaloid forms no definite aurichloride or platinichloride; the picrate forms feathery yellow needles from dilute alcohol, m.p. 114°. The sulphate, on addition of excess of ammonia, when warmed at 100°, gives a play of colours red, reddish-yellow, green, blue (Petit, Compt. rend. 1871, 72, 569). A fragment of the alkaloid dissolved in a drop or two of fuming nitric acid, and evaporated to dryness at 100°, leaves a green residue. Causes contraction of the pupil of the eye—*i.e.* myotic—and when administered internally acts as a powerful poison (*cf.* Cushny, J. Physiol. 1910, 41, 233). Forms a methiodide B·MeI; only one of the three nitrogen atoms is basic (Petit and Polonowsky, *l.c.*). Is oxidised when exposed to air, especially in presence of alkali, forming first *eseroline* $C_{13}H_{18}ON_2$ by loss of carbon dioxide and methylamine, and eventually a red crystalline colouring matter *rubreserine*. When calcium chloride is added to its aqueous solution a fine red colouring matter is also produced. When alkalis act on eserine the alkaloid *calabarine* appears to be formed (*see* below).

Physovenine $C_{14}H_{18}O_3N_2$ occurs in the mother liquors from which eseramine has been crystallised (*see* below). Colourless prisms, m.p. 123°, from dilute alcohol or benzene and light petroleum; very soluble in alcohol, benzene, or chloroform, moderately so in ether, insoluble in water or light petroleum. Salts dissociated by water. Barium hydroxide decomposes it, forming barium carbonate and a red colouring matter. Physovenine appears to be an intermediate product in the formation of eseroline from physostigmine. Powerfully myotic (Salway, *l.c.*).

Eseramine $C_{16}H_{25}O_3N_4$ occurs in the ethereal liquors from which physostigmine has been extracted by dilute sulphuric acid (*see* above), and can be isolated by washing the residue with small quantities of ether and re-crystallising the matter insoluble in ether from alcohol; colourless needles, m.p. 245°; sparingly soluble in ether, chloroform, or benzene, readily so in hot alcohol (Ehrenberg, Verh. Ges. Deut. Naturf. Aertzte, 1893, ii. 102; and Salway, *l.c.*).

In addition to the foregoing the following alkaloids have been stated to occur in Calabar beans, but Salway (*l.c.*), was unable to confirm their presence.

Calabarine. Harnack and Wittkowski state (Arch. expt. Path. Pharm. 1876, 5, 401; 8, 125; 9, 434; 10, 301; 12, 101) that this alkaloid is formed by the action of alkalis on physostigmine, and that it also occurs in Calabar beans. The evidence for its existence is based mainly on evidence obtained from its physiological action, which is stated to be strychnine-like and antagonistic to that of physostigmine. It is probable that 'calabarine' is a mixture of decomposition products of physostigmine (*cf.* Ehrenberg, *l.c.*). *Eseridine* $C_{15}H_{23}O_3N_3$, crystalline (Böhringer and Söhne, Ph. Post. 1888, 21, 663; Eber, Pharm. Zeit. 1892, 37, 483). iso*Physostigmine* $C_{15}H_{21}O_2N_3$ (Ogui, Apoth. Zeit. 1904, 19, 891).

PILOCARPINE AND THE ALKALOIDS OF JABORANDI.

The jaborandi of commerce now consists of the leaves of *Pilocarpus microphyllus* (Stapf.), though the leaves of *P. Jaborandi*, *P. pennatifolius* (Lem.), *P. spicatus* (A. St. Hill), and *P. trachylophus* have also appeared in trade. The drug was examined by Hardy (Bull. Soc. chim. 1875, [ii.] 24, 497), Gerrard (Pharm. J. 1875, [iii.] 5, 865, 965; 1877, [iii.] 7, 225), Harnack and Meyer (Annalen, 1880, 204, 67), Jowett (Chem. Soc. Trans. 1900, 77, 474, 851; 1901, 79, 581, 1331), and Pyman (*ibid.* 1912, 101, 2260; *cf.* Leger and Roques, Compt. rend. 1912, 155, 1088; 1913, 156, 1687). The results of these researches show that *P. microphyllus* leaves contain pilocarpine, *iso*-pilocarpine (β-pilocarpine of Bruhl, Hjelt, and Aschan; pilocarpidine of Petit and Polonowsky (J. Pharm. Chim. 1897, [vi.] 5, 370, 430, 475; 1898, 6, 8), and pilosine, $C_{16}H_{18}O_3N_2$, plates, m.p. 187°. Harnack and Meyer's pilocarpidine (Chem. Zeit. 1885, 628) and jaborine (Annalen, 1880, 204, 67) may occur in *P. Jaborandi* leaves, which are no longer obtainable in commerce. Petit and Polonowsky have stated that *P. spicatus* leaves contain ψ-pilocarpine and ψ-jaborine (*l.c.*). Pilocarpine, *iso*pilocarpine, and pilocarpidine cause contraction of the pupil of the eye and act as sialogogues. Pilocarpine is most, and pilocarpidine least, active. In certain respects they are antagonistic to atropine (*v.* JABORANDI, vol. iii. p. 184).

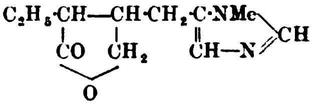
Preparation. The finely-powdered leaves are extracted with alcohol containing hydrochloric acid. The solvent is distilled off, the aqueous residue filtered, neutralised with ammonia and evaporated to a low bulk. Excess of ammonia is then added and the alkaloids extracted with chloroform. The chloroform is distilled off, the residue dissolved in as little water as possible and neutralised with dilute nitric acid. The crystalline nitrates which form are separated into pilocarpine nitrate and *iso*pilocarpine nitrate, by re-crystallisation from alcohol until each is of constant melting-point.

Estimation. A weighed quantity of the finely-powdered drug is extracted in a Soxhlet apparatus with alcohol containing 1 p.c. of ammonia. The alcohol is distilled off and the residue dissolved in water, made alkaline with ammonia if necessary, and extracted with chloroform. The chloroform solution is separated, the solvent distilled off, and the residue dried at 100° and weighed. It represents the total alkaloids. Jowett (Pharm. J. July 29, 1899) has proposed a method for the approximate estimation of pilocarpine in this residue by conversion into the crystalline nitrate and observation of the optical rotation of the product.

Pilocarpine $C_{11}H_{16}O_2N_2$ is a colourless oil, soluble in water, alcohol, or chloroform, b.p. 260° under 5 m.m. pressure, being partially converted into *iso*pilocarpine (*see* below) in the process. Dextrorotatory, $[\alpha]_D + 100{\cdot}5°$; the rotation is reduced by the addition of alkali. The salts crystallise well; the nitrate $B.HNO_3$ forms well-defined prisms, m.p. 178°, the aurichloride $B{\cdot}HAuCl_4$, lemon-yellow needles, m.p. 117°–130° (dry), and the picrate, characteristic long needles, m.p. 147°.

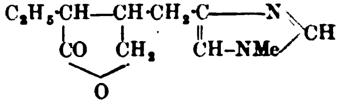
***iso*Pilocarpine** $C_{11}H_{16}O_2N_2$. When pilocarpine is heated alone or with alcoholic soda it is changed into *iso*pilocarpine, which also occurs in *P. microphyllus* and *P. Jaborandi* leaves, and according to Jowett (Chem. Soc. Trans. 1900, 77, 473), is frequently found in commercial pilocarpine nitrate. It is an oil, b.p. 261°/10 mm., $[\alpha]_D = +42{\cdot}8°$ in alcohol. The nitrate $B{\cdot}HNO_3$, m.p. 159°, crystallises in prisms, and is less soluble in alcohol than pilocarpine nitrate (Jowett, *l.c.*). The aurichloride, m.p. 158°–159°, forms lemon-yellow needles.

Reactions and constitution. On solution in alkalis both alkaloids form unstable sodium salts, viz. sodium pilocarpate and sodium *iso*pilocarpate, from which salts of other metals may be prepared. On oxidation with permanganate *iso*pilocarpine produces homopilopic acid $C_8H_{12}O_4$, and pilopic acid $C_7H_{10}O_4$. The former on fusion with potash yields α-ethyltricarballylic acid, and the second, on similar treatment, gives *n*-butyric acid. By distillation with soda-lime *iso*pilocarpine yields 1 : 3- (or 5-) dimethylglyoxaline (Jowett, Chem. Soc. Trans. 1900, 77, 474, 851; 1901, 79, 581, 1331; 1903, 83, 440; *cf.* Pinner and collaborators, Ber. 1900, 33, 1424, 2357; 1901, 34, 727; 1902, 35, 2241). One of the two following formulæ is regarded as representing *iso*pilocarpine—



I.

or



II. *iso*-Pilocarpine (Jowett).

the balance of evidence being in favour of I. (Jowett, Chem. Soc. Trans. 1903, 83, 438; 1905, 87, 794; and Pyman, *ibid.* 1910, 97, 1814; *cf.* Pinner and Schwarz, Ber. 1902, 35, 2441). Pilocarpine is probably a stereoisomeride of *iso*pilocarpine (Jowett, *loc. cit.*).

Pilocarpidine $C_{10}H_{14}O_2N_2$ occurs in *Pilocarpus Jaborandi* leaves, but not in those of *P. microphyllus*, and consequently is not obtainable from the jaborandi leaves of present-day commerce. The alkaloid is liquid, but yields crystalline salts; the hydrochloride has $[\alpha]_D +72°$; the nitrate, m.p. 137°, $[\alpha]_D +73{\cdot}2°$, is much more soluble in alcohol than pilocarpine and *iso*pilocarpine nitrates; the aurichloride, m.p. 124°–125°, is soluble in water. As in the case of pilocarpine, the optical rotation of pilocarpidine is reduced by the addition of alkali (Harnack and Meyer, Chem. Zeit. 1885, 628; Merck, Arch. Pharm. 1898, 236, 141; Jowett, Chem. Soc. Trans. 1900, 77, 474). The name pilocarpidine was erroneously applied by Petit and Polonowsky to *iso*pilocarpine (p. 664).

Jaborine. This amorphous alkaloid may occur in *P. Jaborandi* leaves (Harnack and Meyer, Annalen, 1880, 204, 67). According to Jowett (*l.c.*) commercial jaborine is a mixture of *iso*pilocarpine, pilocarpidine, and possibly pilocarpine, with colouring matter.

Pilosine. *See* under *Pilocarpine* (p. 664).

Piperine $C_{17}H_{19}O_3N$, the alkaloid contained in the fruits of *Piper nigrum* (Linn.), as well as in other plants belonging to the natural order *Piperaceæ, e.g. Piper longum* (Linn.), *P. Clusii* (C. DC.), *P. methysticum* (Forst.), &c. Commercial black and white peppers contain from 5 to 9 p.c. of this alkaloid (*v.* PEPPER, vol. iv. pp. 108, 111.

Preparation. Piperine may be extracted from finely-powdered pepper, preferably white pepper, by means of alcohol. The alcohol is distilled from the solution, and the alkaloid precipitated from the remaining aqueous residue by adding excess of potash, so that the greater part of the resin is dissolved. The base is purified by crystallisation from alcohol.

Another plan is to mix the powdered pepper with milk of lime and boil the mixture for about 15 mins.; it is then evaporated to dryness on the water-bath. The free piperine is extracted from the dry mass by means of boiling ether and crystallised from alcohol (Cazeneuve and Caillot, Bull. Soc. chim. 1877, [ii.] 27, 290). This process is also employed for the estimation of piperine in pepper.

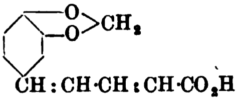
Properties. Monoclinic crystals, m.p. 128°–129°. Slightly soluble in water, more soluble in ether, alcohol, benzene, or chloroform. Optically inactive. An alcoholic solution has a pepper-like flavour. Piperine is a weak base. It is not alkaline, and may be extracted from solutions in dilute acids by indifferent solvents, such as ether. The principal salts are formed by combination with acids in the absence of much water. The platinichloride and mercurichloride are crystalline and insoluble in water; the triiodide $B_2{\cdot}HI,I_2$, formed by adding iodine in potassium iodide to a solution of piperine in alcohol containing hydrochloric acid, forms steel-blue needles.

Reactions and constitution. Piperine dissolves in strong sulphuric acid, forming a dark-red solution. Nitric acid converts the alkaloid into a resinous mass, which dissolves in potash, producing a dark-red solution.

When piperine is heated with aqueous alkalis it is hydrolysed into piperidine and piperic acid

$$C_{17}H_{19}O_3N+H_2O=C_5H_{11}N+C_{12}H_{10}O_4.$$

Piperidine is hexahydropyridine, whilst piperic acid is a derivative of protocatechuic acid having the following constitution—



Piperic acid.

Piperine has been prepared by the action of piperyl chloride on piperidine (Rugheimer, Ber. 1882, 15, 1390), and Ladenburg and Scholz have prepared piperic acid from protocatechuic aldehyde (*ibid.* 1894, 27, 2958). Piperine is therefore piperylpiperidine.

Piperovatine $C_{16}H_{21}O_2N$ occurs in *Piper ovatum* (Vahl.). Forms colourless needles, m.p. 123°, from alcohol by addition of ether. Optically inactive and feebly basic. Heated with water at 160° it gives a volatile base, probably a pyridine derivative, an acid and a substance having an odour of anisole. It is a temporary depressant of motor and sensory nerves and sensory nerve terminations, producing some local anæsthesia. It behaves as a heart poison and stimulates the spinal cord in frogs, causing tetanic spasms somewhat resembling those induced by strychnine (Dunstan (with Garnett), Chem. Soc. Trans. 1895, 67, 94; (with Carr), Chem. Soc. Proc. 1895, 177). It closely resembles *pellitorine* (pyrethrine), the alkaloid of pyrethrum root (*Anacyclus Pyrethrum* [DC.]) (Dunstan and Garnett, *l.c.* 101; *cf.* Buchheim, Arch. expt. Path. Pharm. 1876, 5, 458).

Pituribe, from the Australian plant 'pituri' (*Duboisia Hopwoodii* [F. Muell.]), is probably identical with nicotine (p. 662) (*cf.* Langley and Dickenson, J. Physiol. 1884, 11, 265; Rothera, Bio-Chem. J. 1910, 5, 193).

Protopine $C_{20}H_{19}O_5N$ (*Fumarine, Macleyine*) is widely distributed in plants of the N. O. *Papaveraceæ* and *Fumariaceæ, e.g.* in *Chelidonium majus* (Linn.) (Schmidt and Selle, Arch. Pharm. 1890, 228, 441), *Sanguinaria canadensis* (Linn.) (König and Tietz, *ibid.* 1893, 231, 145, 161), *Bocconia cordata* (Willd.) (Eykman, Rec. trav. chim. 1884, 3, 182), opium (Hesse, Annalen, 1872, S. 8, 318), *Adlumia cirrhosa* (Rafin.), *Glaucium flavum* (Crantz.), *Corydalis* spp., *Dicentra* spp., &c. (*cf.* Schmidt, Arch. Pharm. 1901, 239, 395; 1911, 249, 224; Fischer and Soell, Ph. Ar. 1902, 5, 121; Heyl, Arch. Pharm. 1903, 241, 313; Asahina, *ibid.* 1909, 247, 201; Danckwortt, *ibid.* 1912, 250, 590). Monoclinic crystals, m.p. 207°. Tertiary base. The salts are crystalline; the aurichloride $B{\cdot}HAuCl_4$, amorphous, melts at 182°. Protopine gives with sulphuric acid a blue-violet coloration, changing to green.

Pseudojervine. *See* under *Cevadine* (p. 644).

Psychotrine. *See* under *Emetine* (p. 652).

QUININE AND THE CINCHONA ALKALOIDS.

The barks of the different species of cinchona (*C. officinalis* (Linn.), *C. succirubra* (Pav.) *C. Ledgeriana* (Moens.), *C. Calisaya* (Wedd.), &c.) contain a large number of crystalline and amorphous alkaloids. At the present time most of the cinchona bark of commerce is derived from *Cinchona Ledgeriana* (a cultivated variety), or from hybrids, produced by selection, according to the richness of their barks in quinine, although a certain amount of *C. succirubra* bark is still marketed for galenical use. Statements as to the amount and nature of the alkaloids in barks of particular species have therefore little but historical or academic interest. These alkaloids exist in the bark chiefly as salts of quinic and cinchotannic acids. Closely related to the cinchona alkaloids proper are those derived from *Remijia pedunculata*, of which the most important is cuprëine. The following are the names and formulæ of the principal alkaloids—

Quinine $C_{20}H_{24}O_2N_2$
Quinidine $C_{20}H_{24}O_2N_2$
Hydroquinine $C_{20}H_{26}O_2N_2$
Hydroquinidine $C_{20}H_{26}O_2N_2$
Cinchonine $C_{19}H_{22}ON_2$
Cinchonidine $C_{19}H_{22}ON_2$
Hydrocinchonine (cinchotine) $C_{19}H_{24}ON_2$
Hydrocinchonidine (cinchonamine) $C_{19}H_{24}ON_2$
Quinamine $C_{19}H_{24}O_2N_2$
Conquinamine $C_{19}H_{24}O_2N_2$
Cuprëine $C_{19}H_{22}O_2N_2$

Quinine $C_{20}H_{24}O_2N_2$, the principal crystalline alkaloid contained in the bark (not in the wood) of many species of *Cinchona*. The amount of quinine contained in the different species varies considerably.

C. Ledgeriana (Moens.) bark is said sometimes to contain as much as 11 p.c. of quinine, whilst *C. officinalis* (Linn.), *C. Calisaya* (Wedd.), and *C. succirubra* (Pav.) usually contain from 2 to 5 p.c. On the average, Java cinchona bark of present-day commerce yields from 5 to 7 p.c. of quinine sulphate. The alkaloids which commonly accompany the quinine in these barks are hydroquinine cinchonidine, cinchonine, and quinidine, but the kind and quantity of the accompanying alkaloids vary in the different species.

Preparation. The total alkaloids are first extracted from the bark. Water dissolves for the most part only the alkaloidal quinates, and not the cinchotannates. The cinchotannates may be dissolved by a dilute acid (sulphuric or hydrochloric acid), or they (as well as the quinates) may be decomposed, and the alkaloids liberated by mixing the bark with an aqueous alkali (lime and water). The various processes proposed for the extraction of the total alkaloid from cinchona bark involve the decomposition of the natural salts in one or other of these two ways. Extraction with dilute hydrochloric acid, which was at first largely resorted to, has been almost entirely abandoned, since much colouring matter was dissolved as well as alkaloid, and its complete removal complicated the subsequent operations. On the large scale the finely-powdered bark is mixed with about one-third of its weight of slaked lime and made into a paste with water. The mixture is thoroughly dried at 100°, powdered, and exhausted in an extraction apparatus with boiling petroleum (Landrin, Compt. rend. 1889, 108, 750), alcohol, or amyl alcohol. On the small scale, chloroform, ether, or a mixture of three volumes of benzene with one of amyl alcohol may be employed. The alkaloids are removed from the solvent by agitating it (or, in the case of alcohol, the evaporated residue is similarly treated) with dilute hydrochloric acid, and the alkaloids are precipitated from the clear acid solution by a slight excess of soda or ammonia.

The alkaloids thus obtained from an ordinary commercial specimen of cinchona bark will, as a rule, be chiefly composed of quinine, hydroquinine, cinchonidine, cinchonine, and a little quinidine.

A nearly complete separation of the quinine may be effected by taking advantage of the smaller solubility of quinine sulphate in cold water. The total alkaloid is dissolved in a slight excess of very dilute sulphuric acid, and almost, but not quite, exactly neutralised with dilute soda or ammonia. The solution is heated to 100° and diluted with hot water, so that for each gram of total alkaloid taken there will be about 70 c.c. of solution. On cooling this solution to 15° quinine sulphate will crystallise, whilst nearly the whole of the other alkaloidal sulphates will remain dissolved. The salt thus obtained is recrystallised several times from boiling water. Great care must be taken in the first instance not to leave the liquid more than just perceptibly acid, or the quinine sulphate will be converted into the exceedingly soluble acid sulphate.

The quinine may also be separated, but less satisfactorily, by extracting the total alkaloid with ether, in which the other alkaloids, especially cinchonine, are much less soluble. For the preparation of small quantities of pure quinine the decomposition of herepathite (*see* below) by hydrogen sulphide (de Vrij and Alluard, J. 1864, 445) may be resorted to.

Properties. Amorphous and anhydrous when precipitated by alkalis from solutions of its salts, but crystallises with $3H_2O$ from a solution in dilute alcohol or aqueous ammonia. Crystalline mono- and di-hydrates have also been described, as well as an amorphous hydrate containing $9H_2O$. These hydrates lose the whole of their water by prolonged exposure over sulphuric acid, or at 100°, and more rapidly at 110°–120°. The ordinary trihydrate melts at 57°, and when warmed in dilute alcohol dissolves and deposits long, colourless needles of anhydrous quinine, m.p. 176° (Hesse, Annalen, 1890, 258, 135); 172·8° (corr.) (Lenz, Zeitsch. anal. Chem. 1888, 27, 549). Quinine is very slightly soluble in cold water (1 in 1960 at 15°), but is rather more soluble in hot water, rather less soluble in water in presence of alkalis or ammonia (except when freshly precipitated; it is readily soluble in alcohol, ether, or chloroform. It dissolves in hot benzene and separates on cooling in crystals containing 1 mol. of the solvent.

The aqueous solution is bitter and alkaline to litmus. The following quantities of quinine trihydrate are dissolved by 100 parts of the respective solvents at 15°; absolute alcohol, 88·2 parts; chloroform, 51·9 parts; ether, 4·42 parts. Also soluble in carbon disulphide, benzene, amyl alcohol, or light petroleum. Quinine shows lævorotation varying in amount with the concentration and the solvent; for the anhydrous alkaloid $[\alpha]_D^{15} = -158°$. For determination of the rotatory power in alcohol and ether *see* Hesse, Annalen, 1875, 176, 285; 1876, 182, 128; Oudemans, *ibid.* 1876, 182, 44.

Quinine readily dissolves in dilute acids forming salts. The acid solutions of the salt show a magnificent blue fluorescence if the acid used contains oxygen (*e.g.* sulphuric acid), but not if the acid contains no oxygen (*e.g.* hydrochloric acid). In the formation of salts quinine behaves as a diacidic base, unlike most of the vegetable alkaloids, which are monacidic. The salts ordinarily met with, however, contain 1 mol. prop. of a monobasic acid to 1 of quinine, or 1 mol. prop. of a dibasic acid to 2 of quinine, &c. Nearly all the quinine salts crystallise, and are readily soluble in water or alcohol. The hydrochloride $B{\cdot}HCl,2H_2O$, prepared by neutralising the alkaloid with dilute hydrochloric acid, crystallises in long, silky needles, soluble in water, alcohol, or chloroform. Its solutions are lævorotatory. The dihydrochloride $B{\cdot}2HCl$ is produced when dry hydrochloric acid gas combines with quinine, or when the disulphate is decomposed in solution by barium chloride. On evaporation of its solution it is obtained in hard needles. The normal sulphate or diquinine sulphate $B_2{\cdot}H_2SO_4,8H_2O$, sometimes called 'bisulphate,' is the ordinary commercial sulphate of quinine. It is prepared by exactly neutralising warm dilute sulphuric acid with the alkaloid. When the crystals are exposed to air they effloresce and gradually lose $6H_2O$. The salt as usually met with contains about $7\frac{1}{2}H_2O$. Quinine sulphate is slightly soluble in water (1 in 740 at 15°), and differs in this respect from the normal sulphates of the other principal cinchona alkaloids, all of which are more soluble. In boiling water quinine sulphate is far more soluble (1 in 30), and may readily be obtained in crystals by cooling the solution. The aqueous solution is very bitter and slightly fluorescent. Alcohol dissolves the sulphate much more easily than water (1 in 65 at 15°; 1 in 6 at b.p.). The salt is slightly soluble in chloroform (1 in 1000) and almost insoluble in ether. Dilute acids dissolve large quantities of quinine sulphate; sulphuric acid converts it into the very soluble acid sulphate $B_2(H_2SO_4)_2$ or $B{\cdot}H_2SO_4$.

Quinine sulphate, like the alkaloid, is lævorotatory. In alcohol at 15°, $[\alpha]_D = -166{\cdot}36°$; for the anhydrous sulphate in water $[\alpha]_D = -233{\cdot}75°$ (Hesse).

The salt of commerce is liable to be impure from the presence of the sulphates of other cinchona alkaloids. It may be purified by recrystallisation from water several times, or, better, by dissolving 1 part of the commercial salt in about 30 parts of hot water rendered just acid with sulphuric acid. The crystals which separate on cooling are washed with cold water and dried in the air (Hesse, Annalen, 1880, 205, 218). For methods of estimating the amount of pure salt in the commercial sulphate, *see* ***Estimation of quinine*** (p. 669).

The acid sulphate or monoquinine sulphate $B{\cdot}H_2SO_4,7H_2O$ is produced when the normal sulphate is dissolved in dilute sulphuric acid (Hesse, *ibid.* 1873, 166, 221; 1875, 176, 214). The rhombic crystals effloresce in air and lose their water at 100°. The salt is very soluble in water (1 in 11 at 13°; 1 in 8 at 22°); less soluble in alcohol. The aqueous solution is extremely bitter and exhibits an intense blue fluorescence, which is perceptible in very dilute solutions. The acid sulphates of cinchonidine and cinchonine do not produce this effect, but it is observed with the acid sulphate of quinidine. By dissolving the acid sulphate in sulphuric acid the "tetrasulphate" containing an additional proportion of sulphuric acid $B{\cdot}2H_2SO_4,7H_2O$ may be obtained (Hesse, Annalen, 1873, 166, 222).

In consequence of its marked antipyretic and tonic action quinine is a valuable therapeutic agent. A large proportion of the quinine taken internally is excreted unchanged in the urine.

Reactions. The most striking qualitative reaction of quinine is that known as the thalleioquin (*thallos*, a young twig), colour reaction. It is observed when weak chlorine-water or bromine-water is gradually added to an acidified solution of quinine sulphate, until a permanent, faint yellow coloration is perceptible; excess of the halogen must be avoided. Ammonia solution is at once added to this liquid, drop by drop, when a dark-green coloration or precipitate makes its appearance. If the green liquid is acidified its colour changes to red. This reaction, which may be obtained with dilute solutions, is also given by some other alkaloids of this group, notably by quinidine, but cinchonine and cinchonidine do not exhibit it. Ammonia precipitates the alkaloid from solutions of its salts, the precipitate being soluble in excess; quinidine and cinchonidine are less soluble in solution of ammonia; cinchonine almost insoluble. Potash and soda also precipitate salts of quinine, but the alkaloid is only slightly dissolved by excess of these alkalis. The precipitated quinine is readily soluble in ether, quinidine is less soluble, cinchonidine still less soluble, whilst cinchonine is nearly insoluble.

When an alcoholic solution of quinine sulphate, acidified with dilute sulphuric acid, is mixed with an alcoholic solution of iodine, a reddish precipitate is thrown down, which dissolves when the liquid is heated, and on cooling separates in iridescent crystals, which are green by reflected light, and red by transmitted light. This substance is an iodosulphate of quinine or periodide of quinine sulphate $[B_4(H_2SO_4)_3(HI)_2I_4,6H_2O]$, and has been called 'herepathite,' after its discoverer Herepath. Similar compounds may be formed from the sulphates of other cinchona alkaloids; and, since they are more soluble than the quinine compound, De Vrij has proposed a method of estimating quinine in which the herepathite is collected and weighed, when it will represent 55·055 p.c. of its weight of quinine (J. Pharm. Chim. 1875–1876, [iii.] 6, 461).

Moderately concentrated solutions of quinine salts are precipitated by ammonium oxalate, the crystalline quinine oxalate $(B_2{\cdot}H_2C_2O_4,6H_2O)$ being sparingly soluble.

Sodium tartrate, or Rochelle salt (potassium sodium tartrate), in aqueous solution precipitates moderately concentrated solutions of quinine salts. The quinine tartrate $B_2{\cdot}H_2C_4H_4O_6,H_2O$ is much less soluble than the quinidine and cinchonine tartrates, but is rather more soluble than cinchonidine tartrate. These facts are utilised in the separation and estimation of quinine and cinchonidine.

Quinine is remarkable in forming a large number of compounds, many of which are crystalline, with different organic bodies, hydrocarbons of the benzene series, phenols, aldehydes, carbamides, &c.

Detection. Quinine may be detected by means of the properties and reactions described above; the fluorescence of solutions of the acid sulphate, the solubility of the alkaloid in ether, and the thalleioquin reaction being especially useful.

Assay of cinchona bark. For the assay of cinchona bark a large number of processes have been devised. For bark used for the manufacture of galenical preparations the determination of the total alkaloids is generally sufficient, but in the British Pharmacopœia a certain proportion of quinine and cinchonidine taken together is specified, and in that of the United States a certain proportion of ether-soluble alkaloids (quinine, cinchonidine, and quinidine) is prescribed.

The British Pharmacopœia, 1898, gives the following method: 20 grms. of the bark (*C. succirubra*) in No. 60 powder are mixed with 6 grms. of slaked lime and the whole moistened with 20 c.c. of water and allowed to stand for 2 hours. This is transferred to a flask provided with a reflux condenser and boiled with 130 c.c. of benzolated amylic alcohol (benzene 3 vols., amyl alcohol 1 vol.) during 30 mins. The liquid is filtered off and the treatment repeated twice, the mixture of bark and lime being finally transferred to the filter and washed with the solvent until exhausted. The total filtrate, still warm, is placed in a separator and shaken with 2 c.c. of dilute hydrochloric acid (sp.gr. 1·052), diluted with 12 c.c. of water, the acid liquor withdrawn, and the extraction continued with water acidified with hydrochloric acid until all the alkaloids have been extracted. The total acid liquid is then just neutralised with ammonia and evaporated to 16 c.c. To this 1·5 grm. of sodium potassium tartrate, dissolved in 3·0 grms. of water, are added and the mixture stirred well and set aside for 1 hour. The precipitated quinine and cinchonidine tartrates are then collected on a tared filter, washed, dried, and weighed. The precipitate contains $\frac{8}{10}$ of its weight of alkaloids, and this multiplied by 5 gives the percentage of quinine and cinchonidine in the bark. To the mother liquor and washings ammonia solution is added in slight excess and the precipitate collected, washed, dried, and weighed. This weight multiplied by 5 gives the percentage of 'other alkaloids' in the bark, and the sum of the two gives the percentage of total alkaloids. The bark should contain 5–6 p.c. of total alkaloids, of which at least half should be quinine and cinchonidine.

The U.S. Pharmacopœia (8th revision) process is as follows: 15 grms. of bark (*C. Ledgeriana*, *C. Calisaya* or *C. officinalis* or hybrids of these) in No. 80 powder is shaken with 250 c.c. of ether (sp.gr. 0·720 at 25°) and 50 c.c. of chloroform and set aside for 10 mins. in a stoppered flask or bottle. 10 c.c. of ammonia solution (sp.gr. 0·958 at 25°) are then added and the mixture shaken frequently during 5 hours. 15 c.c. of water are then added and the mixture shaken to cause the powder to settle easily. 200 c.c. of the clear supernatant liquid (10 grms. of bark) are then decanted into a separator, 15 c.c. of N-sulphuric acid added, and the whole shaken vigorously. The aqueous layer is withdrawn, and the extraction continued with (*a*) 5 c.c. of N-acid and 5 c.c. of water, and (*b*) 5 c.c. of water. The combined acid liquors are filtered into a measuring cylinder and the filter paper washed with enough water to make the contents of the cylinder measure 50 c.c. Of this 25 c.c. are placed in a separator and 25 c.c. of a mixture of chloroform (3 vols.) and ether (1 vol.), followed by 5 c.c. of ammonia solution added and the whole shaken. The chloroform-ether solution (lower layer) is withdrawn and the extraction continued with (*a*) 20 c.c. of the chloroform-ether mixture, and (*b*) 10 c.c. of chloroform. The mixed chloroform-ether extracts are run into a tared flask, the solvent distilled off, the residue re-dissolved in 3 c.c. of ether, the solvent evaporated and the residue dried at 110° and weighed. The weight multiplied by 20 gives the percentage of total alkaloids, which should not be less than 5 p.c.

The second 25 c.c. of solution is mixed in a separator with 25 c.c. of ether and 5 c.c. of ammonia solution. The whole is cooled below 20° if necessary, and shaken moderately during 2 mins., and then set aside during 10 mins. at 15°. The lower aqueous layer is rejected and the ethereal solution transferred to a tared beaker. The separator is rinsed out with 5 c.c. of ether and this added to the beaker. The solvent is evaporated and the residue dried at 110° and weighed. This weight multiplied by 20 gives the percentage of ether-soluble alkaloids (quinine, quinidine, and cinchonidine), which should be at least 4 p.c.

The German Pharmacopœia (1910 ed.) prescribes a method on the same lines as that of the United States, but the total alkaloids only are determined, and this is done by titration, using hæmatoxylin as indicator.

Estimation of quinine in cinchona bark. Most of the cinchona bark which comes into commerce is used for the manufacture of quinine sulphate, and consequently the estimation of quinine in such bark is of the first importance. The methods used are very varied, and recently an association of cinchona planters in Java has offered a prize for a method, which will give accurate results, and can be recommended for general adoption.

The chief methods which have been proposed for the separation and estimation of quinine in the total alkaloids, depend upon the smaller solubility of the quinine sulphate in water, and since the usual object is to ascertain the yield of quinine sulphate obtainable from the bark, it is probable that such methods are best for this purpose.

A quantity (1–5 grms.) of the total alkaloid (isolated as described above) is weighed in a beaker, a small quantity of warm water is added, and the mixture titrated with decinormal sulphuric acid until it is just acid to litmus. The solution is heated for about 15 mins. on the water-bath, and at the end of this time should still be feebly acid. The warm liquid is now titrated to exact neutrality with decinormal soda solution. The number of c.c. of soda solution required deducted from the number of c.c. of acid used, gives the number of c.c. of acid neutralised by the total alkaloid, and this number multiplied by 0·03 ought to give a close approximation to the amount in grams of total alkaloid originally taken.

The amount of total alkaloid having been thus verified by titration, the neutralised liquid is diluted with water until its weight is 70 times that of the total alkaloid, and then heated to about 90° for 5 mins. It is now cooled to 15°, and kept at this temperature for half an hour. If crystals have not separated there is not more than 8 p.c. of quinine in the total alkaloid. As a rule, crystals will be deposited, and these must be collected on a small weighed filter and washed with sufficient cold water (15°) to make the total weight of filtrate equal to 90 times that of the total alkaloid present. The crystals are dried at 100° and weighed as anhydrous quinine sulphate. To this weight must be added 0·12 p.c. of the weight of the filtrate and washings, in order to compensate for the loss of the sulphate through its solubility in water at 15°.

Estimation of quinine and impurities in commercial quinine sulphate. Commercial quinine sulphate is rarely, if ever, quite pure. That intended for medicinal use should not afford any appreciable reaction for cinchonine, quinidine, cupreine, or amorphous alkaloid, and should not yield more than 3 p.c. of crystals of cinchonidine (B. P. 1898). The principal impurities are cinchonidine and hydroquinine sulphates, but there may also be present quinidine and cinchonine sulphates, whilst if the alkaloid has been derived from cuprea bark, sulphate of cupreine may be found.

The various methods of examining commercial quinine sulphate for the sulphates of other cinchona alkaloids depend either on the greater solubility of the quinine in a definite volume of aqueous ammonia (Kerner's test), or in a definite volume of ether (the so-called 'Liebig's test'), or on a combination of these two facts (Hesse's test).

The German Pharmacopœia (1910) gives the following directions for the application of Kerner's test. Two grms. of the quinine sulphate dried completely at 40°–50°, are mixed with 20 c.c. of water, and the mixture kept with occasional agitation for 30 mins. at 60°–65°; the mixture is then kept at 15° during 2 hours, poured through linen, and finally filtered through filter paper; 5 c.c. of the clear solution are placed in a test-tube, and 4 c.c. of aqueous ammonia (rel. dens. 0·959) added. The precipitate formed should dissolve completely on shaking.

The French Codex (1909) directs that 1 grm. of the hydrated salt should be dissolved by boiling with 30 c.c. of water, after which the liquid must be cooled to 15°, and kept at this temperature with agitation for 30 mins. 5 c.c. is specified as the quantity of ammonia solution required to re-dissolve the precipitate. The U.S. Pharmacopœia method (8th revision) is essentially the same as that of the German Pharmacopœia, but 7 c.c. of ammonia solution is added all at once, and under these conditions the sulphate is required to give a clear solution. Tutin (Pharm. J. 1909, [iv.] 29, 600) has critically examined these methods, and recommends a modified form of the French Codex method, which, however, is only applicable to quinine sulphate: he suggests 6 c.c. of ammonia solution as ensuring a reasonable degree of purity in the salt.

A modification of this method is adopted in the British Pharmacopœia (1898) for the detection of cinchonidine and cinchonine. 4 grms. of the quinine sulphate are dissolved in 120 c.c. of boiling water; the solution is cooled slowly to 50° with frequent stirring, and filtered from the quinine sulphate, which has crystallised. The filtrate is concentrated by evaporation to 10 c.c. or less and placed in a stoppered flask, and when cold 10 c.c. of ether (better, purified ether, Tutin, *l.c.*), and 5 c.c. of ammonia (sp.gr. 0·959) are added. The flask is set aside in a cool place for 24 hours and the separated crystals of cinchonidine with cinchonine and a little quinine are collected, washed with a little ether, dried and weighed. They should not amount to more than 0·12 grm. According to Tutin (*l.c.*) 3 p.c. of cinchonidine may be detected by this method if purified ether is used. Quinidine, if present, would not be separated in the foregoing test, and therefore the British Pharmacopœia includes the following method, which is based on the fact that quinidine sulphate is more soluble in water than quinine sulphate, and that of the two hydriodides the quinidine hydriodide is less soluble in water. 1 grm. of the quinine sulphate is dissolved in 30 c.c. of boiling water and the solution cooled and filtered. To the filtrate, a solution of potassium iodide (20 grms. in 200 c.c.) is added and a little alcohol to prevent precipitation of amorphous hydriodides. The precipitated quinidine hydriodide is collected, washed with a little water, dried, and weighed. Its weight is approximately equivalent to that of the crystallised quinidine sulphate. None or only traces should be found.

The *cupreine sulphate* (*see Cupreine*) may be found and estimated by taking advantage of the slight solubility of cupreine in ether. The cupreine sulphate, being but sparingly soluble in cold water, will be mixed with the recrystallised quinine sulphate which was removed in testing for cinchonidine and cinchonine (*v. supra*). The quinine and cupreine sulphates are mixed with 25 c.c. of ether and 6 c.c. of aqueous ammonia (10 p.c.). After shaking the mixture the ethereal solution is removed and added to the ethereal liquid obtained in the test for cinchonidine and cinchonine, out of which these alkaloids had crystallised. The ethereal solutions are now agitated with about 6 c.c. of aqueous soda (10 p.c.), which dissolves the cupreine. The ether is removed, the alkaline solution washed with more ether, and finally heated to 100°. The hot liquid is exactly neutralised with dilute sulphuric acid, and when the solution is cold the cupreine sulphate which has crystallised out is collected, dried, and weighed. None or only traces should be obtained.

For cinchonine and amorphous alkaloids the B. P. 1898, prescribes the following test: 1 grm. of the quinine sulphate is dissolved in 30 c.c. of boiling water and 1 grm. of sodium potassium tartrate added. The mixture is cooled with frequent stirring and filtered. The filtrate after evaporation to a small bulk should give little or no precipitate with solution of ammonia.

For the estimation of hydroquinine Howard (Pharm. J. 1896, [iv.] 3, 505) recommends dissolving the ether-soluble alkaloids obtained in the B. P. test for cinchonidine and cinchonine (*v. supra*) in dilute sulphuric acid, adding to this solution 4 p.c. permanganate solution so long as the latter is rapidly decolorised. The manganese dioxide is filtered off, the filtrate made alkaline with ammonia solution and shaken out with ether. The residue left on evaporating the ether is dissolved in dilute sulphuric acid, then just neutralised with ammonia and the crystals, which separate, dried and weighed.

For a comparison of the various methods of examining commercial quinine sulphate, *see* Lenz, Zeitsch. anal. Chem. 1888, 27, 549.

Quinidine or **Conquinine** $C_{20}H_{24}O_2N_2$. This isomeride of quinine is contained in small quantity in most of the ordinary cinchona barks, especially in *C. pitayensis* (Wedd.) and *Cinchona Calisaya*, which sometimes contain as much as 3 p.c. (Hesse, Annalen, 1874, 174, 338). It is most conveniently procured from the amorphous mixture of cinchona alkaloids commercially known as 'quinoidine.' The powdered 'quinoidine' is extracted with ether, and the ethereal solution shaken with dilute sulphuric acid. The neutralised aqueous liquid is precipitated with a strong solution of Rochelle salt, and the concentrated filtrate, decolorised if necessary with charcoal, precipitated with a strong solution of potassium iodide. The impure quinidine hydriodide is washed and dissolved, and the alkaloid precipitated from the solution with ammonia. The precipitated alkaloid is now dissolved in dilute acetic acid, and, if necessary, again decolorised with charcoal. The alkaloid is then reprecipitated with ammonia and crystallised from boiling alcohol (Hesse, Annalen, 1868, 146, 357; 1873, 166, 232).

Properties. Large prismatic crystals containing $2\frac{1}{2}H_2O$, which lose $\frac{1}{2}H_2O$ on exposure to air, or on recrystallising from ether, and $1H_2O$ on crystallising from boiling water (Hesse, Ber. 1877, 10, 2154).

The anhydrous alkaloid melts at 171·5° (corr.) (Lenz, Zeitsch. anal. Chem. 1888, 27, 571). Dextrorotatory $[\alpha]_D = +274{\cdot}7°$ in alcohol, 1 vol. and chloroform 2 vols. (Lenz), +243·5° (Rabe). Very slightly soluble in water (1 in 2000 at 15°; 1 in 750 at 100°), more soluble in alcohol (1 in 26 at 20°), and in ether (1 in 22 at 20°); also dissolved by amyl alcohol, benzene, or chloroform, but not appreciably by light petroleum. Dilute acids dissolve the alkaloid abundantly and, like quinine, the solutions, if acid with sulphuric acid or other oxygenated acid, exhibit a blue fluorescence. Like quinine, quinidine is a diacidic base, but only its normal salts are usually met with. The normal sulphate $B_2{\cdot}H_2SO_4,2H_2O$ is more soluble in cold water than the quinine salt (1 in 100 at 15°), and also in chloroform (1 in 20 at 15°). The acid sulphate $B{\cdot}H_2SO_4$ is very soluble in water, and its solution is highly fluorescent. The hydriodide $B{\cdot}HI$ is an important salt, since it is much less soluble in water (1 in 1250 at 15°) than the hydriodides of the other cinchona alkaloids, and is therefore employed in isolating and in estimating quinidine. It is precipitated at once, or from dilute solutions after standing and stirring, as a crystalline powder when potassium iodide is added to a neutral or slightly acid solution of a quinidine salt. In presence of much acid the soluble dihydriodide $B{\cdot}(HI)_2$ is produced.

Quinidine and its salts have a very bitter taste, and exert a physiological and therapeutic action very like that of quinine.

Reactions. The chief reactions of quinidine resemble those of quinine. It affords the thalleioquin colour reaction (p. 667); its derivatives and decomposition products are identical with those of quinine, of which it is a stereoisomeride, the carbon atom concerned being that numbered 3 in the general formula (p. 673) (Rabe, Annalen, 1910, 373, 85).

Detection and estimation. Quinidine may be detected by the fluorescence of acid solutions of its salts, by its affording the thalleioquin reaction, by solutions of its salts not being precipitated by solution of Rochelle salt (distinction from quinine and cinchonidine), and by the formation of the insoluble hydriodide, &c., and by other properties described above. For the estimation of the alkaloid in cinchona bark advantage may be taken of the solubility of the normal sulphate in chloroform or cold water, the solubility of quinidine tartrate, and the formation of the hydriodide, which is collected and weighed. The quinine and cinchonidine, having been removed from the total alkaloids as tartrates (*see Estimation of quinine*, pp. 668–9), the filtrate, somewhat concentrated, is precipitated with a saturated solution of potassium iodide. After standing for an hour the quinidine hydriodide is collected, washed with a little cold water, dried, and weighed.

For the estimation of quinidine in commercial sulphate of quinine, *see* under *Estimation of Quinine* (p. 669).

Cinchonine $C_{19}H_{22}ON_2$ is an alkaloid commonly occurring in cinchona bark to the extent of about 0·2–2 p.c. It may be readily prepared from the mother liquor remaining from the preparation of quinine (p. 666). This solution, which contains cinchonine sulphate, is precipitated with soda, and the precipitate crystallised from its solution in alcohol. The alkaloid thus obtained is purified by converting it into the normal sulphate, which is repeatedly crystallised from water (Hesse, Annalen, 1862, 122, 226); or the precipitate produced by the soda may be dried and digested with cold ether in which cinchonine is very slightly soluble. The residue is crystallised from alcohol.

Properties. Anhydrous, monoclinic prisms (from alcohol), or amorphous when precipitated, m.p. 264° (*cf.* Lenz, Zeitsch. anal. Chem. 1888, 27, 572; Hesse, Annalen, 1880, 205, 211). At a higher temperature it sublimes with some decomposition. Almost insoluble in water (1 in 3670 at 20°), slightly soluble in ether (rel. dens. 0·730, 1 in 371 at 10°) or benzene, more soluble in alcohol (rel. dens. 0·852, 1 in 126 at 20°), or chloroform (1 in 356 at 17°), but most readily in a mixture of chloroform and alcohol which dissolves more than either liquid alone. Soluble in amyl alcohol, nearly insoluble in aqueous ammonia, in light petroleum, or absolute alcohol. Readily soluble in dilute acids, but the solutions are not fluorescent. Dextrorotatory, $[\alpha]_D^{17°} = +223{\cdot}3°$ (Oudemans, Annalen, 1876, 182, 44; *cf.* Rabe, *ibid.* 1910, 373, 85).

Cinchonine is a diacidic base, and the ordinary salts correspond in composition with those of quinine. The normal sulphate $B_2{\cdot}H_2SO_4,2H_2O$ is soluble in water (1 in 70 at 15°; 1 in 14 at 100°); soluble also in alcohol (1 in 6 at 15°) or chloroform (1 in [illegible]0 at 15°). The acid sulphate $B{\cdot}H_2SO_4,4H_2O$ is soluble in water, but, unlike the correspond-quinine and quinidine salts, its aqueous solutions are not fluorescent, although commercial specimens of the sulphate, when dissolved in dilute sulphuric acid, are usually slightly fluorescent owing to the presence of quinine or quinidine. The salts of cinchonine are very bitter, and appear to exert the same physiological and therapeutic action as quinine, although much less powerfully.

Like quinine, cinchonine combines with phenols and certain other organic compounds.

Reactions. The reactions of cinchonine are similar to those of quinine. It does not, however, afford the thalleioquin colour reaction (p. 670).

In its combinations with methyl iodide, cinchonine, like quinine, acts as a tertiary diamine.

A large number of isomerides of cinchonine, produced by the action of sulphuric acid or other agents on the alkaloid, are known.

Detection and estimation. Cinchonine is readily distinguished from quinine and quinidine by not giving the thalleioquin reaction, as well as by other properties described above. From cinchonidine, which it resembles in not giving the colour reaction, it may be distinguished by its dextrorotation, its slight solubility in aqueous ammonia or ether, and also by the solubility of its normal sulphate in chloroform. The amount of cinchonine contained in the total alkaloids of cinchona bark may be estimated in the filtrate and washings from which the quinidine has been separated as hydriodide (*see* p. 670), by precipitating it with soda, and digesting the dried precipitate with a small quantity of ether in order to dissolve the amorphous alkaloid. The residue is dried and weighed as cinchonine.

For the detection and estimation of cinchonine n commercial sulphate of quinine, *see* under *Estimation of Quinine* (pp. 668–9).

Cinchonidine $C_{19}H_{22}ON_2$, an isomeride of cinchonine, found in most varieties of cinchona bark to the extent of from 0·5 to 5 p.c. Cinchonidine sulphate has been used in medicine as a substitute for quinine.

Preparation. The total alkaloids having been extracted from the cinchona bark (*see* under *Quinine*, p. 666), and the crystallised quinine sulphate separated, the aqueous solution (containing cinchonidine, cinchonine, and quinidine sulphates) is precipitated with ammonia in slight excess, and the precipitate repeatedly extracted with cold ether. The ethereal solution (containing cinchonidine and quinidine) is shaken with dilute hydrochloric acid, when the alkaloidal hydrochlorides pass into the aqueous liquid, which is neutralised, and the cinchonidine precipitated as tartrate by the addition of solution of Rochelle salt. The precipitate is dissolved in hydrochloric acid and precipitated with ammonia in slight excess. The alkaloid thus obtained is crystallised from its solution in boiling alcohol, then converted into the normal sulphate, which is crystallised from water. The crystallised salt is dissolved in 25 parts of boiling water, and the solution cooled to 35°, when any crystals which may have separated are removed and twice recrystallised. By precipitating a solution of this salt with ammonia and crystallising the precipitate from alcohol, pure cinchonidine is obtained (Hesse, Annalen, 1865, 135, 333; 1880, 205, 196).

The commercial sulphate of cinchonidine may be purified by this process. It generally contains small quantities of the sulphates of other cinchona alkaloids, especially quinine and homocinchonidine, an isomeride of cinchonidine which occurs with it in cinchona barks (Hesse, *ibid.* 1880, 205, 203).

Properties. Anhydrous prismatic crystals, which melt at 207·2° (corr.) (Lenz, Zeitsch. anal. Chem. 1888, 27, 564), 200°–201° (Hesse, Ber. 1881, 14, 1888). Slightly soluble in cold water. Soluble in alcohol (1 in 16·3 at 13°), or ether (1 in 188 at 15°). Readily soluble in chloroform or amyl alcohol. Slightly soluble in aqueous ammonia. Very soluble in dilute acids. Lævorotatory, $[\alpha]_D = -107{\cdot}48°$ in alcohol (Hesse, Annalen, 1875, 176, 219; 1876, 181, 137; *cf.* Skraup, *ibid.* 1879, 199, 365).

Cinchonidine is a diacidic base, but is monacidic in the salts usually met with. The normal sulphate $B_2{\cdot}H_2SO_4,6H_2O$ is used in medicine. It is readily soluble in hot water, but only sparingly in cold (1 in 97·5 at 12°; 1 in 67 at 22°). The acid sulphate $B{\cdot}H_2SO_4,5H_2O$ is very soluble in water. Its solutions are not fluorescent.

Cinchonidine and its salts are very bitter. Their therapeutic action is similar to, but weaker than, that of quinine. The administration of large doses of cinchonine or cinchonidine, but especially the latter, is said to be attended with danger.

Reactions. The principal reactions of cinchonidine resemble those of its stereoisomeride cinchonine. By the action of phosphorus pentachloride the chloro derivative $C_{19}H_{21}N_2Cl$, isomeric with the corresponding cinchonine derivative, is obtained. Although this 'chloride' is isomeric, and not identical with that of cinchonine, it furnishes the same cinchenine (p. 672) when acted on by potash.

The products of the oxidation of cinchonidine by nitric acid and chromic acid are the same as those afforded by cinchonine.

Detection and estimation. Cinchonidine is readily distinguished from quinine and quinidine by not affording the thalleioquin reaction, and in its acid salts not being fluorescent. It differs from cinchonine in its greater solubility in ether, as well as by the slight solubility of its tartrate, &c. It may be identified by the properties described above. Cinchonidine may be estimated in the total alkaloids from cinchona bark by precipitating the liquid from which the quinine has been removed by crystallisation as sulphate, with a strong solution of Rochelle salt, when the cinchonidine tartrate is precipitated. After standing some time the precipitate is collected, dried, and the anhydrous tartrate weighed. Another method consists in determining the amount of quinine in a portion of the total alkaloids, by crystallisation as sulphate, and in a second portion of the total alkaloids, precipitating the quinine and the cinchonidine as tartrates (*see Estimation of quinine*, pp. 668 9). The amount of quinine sulphate already found is then calculated into tartrate, and this quantity is deducted from the weight of the mixed tartrates; the remainder is the amount of cinchonidine tartrate.

It has also been proposed to separate quinine and cinchonidine (liberated from the tartrates) by dissolving out the quinine with ether, but the method does not afford accurate results, since the solubility of cinchonidine in ether is increased by the presence of quinine, owing apparently to the formation of a compound of the two alkaloids.

Cf. Hesse, Annalen, 1880, 205, 217; Pharm. J. 1884–1885, [iii.] 15, 869; 1886, [iii.] 16, 818; Schäfer, Zeitsch. anal. Chem. 1887, 26, 655; Koppeschaar, *ibid.* 1885, 24, 362; Davies, Pharm. J. 1885–1886, [iii.] 16, 358; Paul, *ibid.* 1886, [iii.] 16, 361.

For other information respecting the estimation of cinchonidine in commercial sulphate of quinine, *see* under *Estimation of Quinine.*

Constitution of quinine, quinidine, cinchonine, and cinchonidine. Comparison of the linear formulæ of these four alkaloids shows that they form two pairs of isomerides, of which the second two differ from the first two by containing $-OCH_2$ less, indicating that quinine and quinidine are methoxyl derivatives of cinchonine, cinchonidine, or one of their isomerides. The single oxygen atom in cinchonine and cinchonidine is present as hydroxyl, whilst quinine and quinidine contain their two oxygen atoms in the form of hydroxyl- and methoxyl- in both cases. Since the four alkaloids have a common nucleus it is convenient to discuss their constitutions together. A great deal of work has been expended on the chemistry of these alkaloids by Skraup, Koenigs, von Miller, and Rabe. The most fruitful lines of work have been (1) investigation of the products of hydrolysis of their 'chlorides,' and (2) a study of the oxidation products of the alkaloids.

Hydrolysis of the Chlorides. When quinine or cinchonine is treated in chloroform solution with phosphorus pentachloride, the hydroxyl group in each case is replaced by a chlorine atom with the formation of quinine chloride $C_{20}H_{23}ON_2Cl$ and cinchonine chloride $C_{19}H_{21}N_2Cl$ respectively. These chlorides, on treatment with alcoholic potash, each lose 1 mol. of hydrogen chloride forming quinenine

$$C_{20}H_{22}ON_2$$

and cinchenine $C_{19}H_{20}N_2$ respectively, and these two products are hydrolysed by phosphoric acid in the following manner:—

Quinenine gives *p*-methoxylepidine and meroquinenine.

Cinchenine gives lepidine and meroquinenine.

Oxidation by Permanganate. Quinine yields quininic acid, cincholoiponic acid, and loiponic acid.

Cinchonine yields cinchoninic acid, cincholoiponic acid, and loiponic acid.

Loiponic acid is a product of the oxidation of cincholoiponic acid, and may therefore be neglected for the present purpose.

Quininic acid $C_{11}H_9O_3N$ is 6-methoxy-4-carboxyquinoline.

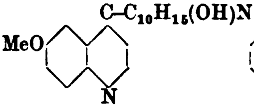
Cinchoninic acid $C_{10}H_7O_2N$ is 4-carboxyquinoline.

Methoxylepidine $C_{11}H_{11}ON$ is 6-methoxy-4-methylquinoline.

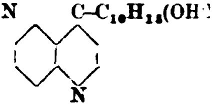
Lepidine $C_{10}H_9N$ is 4-methylquinoline.

The occurrence of these four substances in the oxidation and hydrolytic products clearly establishes the existence in quinine of a methoxymethylquinoline nucleus and in cinchonine of a methylquinoline nucleus.

The remaining portion of the molecule mu be identical both in quinine and cinchonin since it furnishes the same products on oxidat (cinchloiponic and loiponic acids) and on hydr lysis (meroquinenine). This residual portion the molecule has been the subject of mar investigations. It is conveniently spoken of the 'second half,' and is represented by th linear portion of the following formulæ—

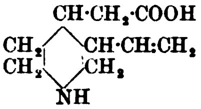


Quinine.

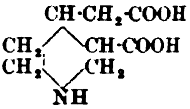


Cinchonine.

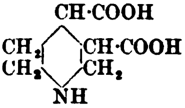
Meroquinenine $C_9H_{15}O_2N$, produced by th hydrolysis both of quinenine and cinchenine, also formed as an intermediate product in th oxidation of quinine and cinchonine. further oxidation it yields *cincholoiponic ac* $C_8H_{13}O_4N$, which also occurs in the oxidati products of the two parent alkaloids, and th in turn on oxidation yields *loiponic acid* $C_7H_{10}O_4$ which is hexahydropyridine-3 : 4-dicarboxyl acid. These three products are, therefor probably related as follows—



Meroquinenine.



Cincholoiponic acid.



Loiponic acid.

The nature of these oxidation products the 'second half,' shows that the latter mus include a heterocyclic ring containing nitrogen This second heterocyclic ring cannot, howeve consist of a reduced pyridine ring with si chains, since quinine and cinchonine are bo ditertiary bases. Further, when cinchenin (*see* above) is heated with hydrobromic acid 180° it loses a molecule of ammonia and form apocinchenine in which the quinoline nucleu still intact, although the 'second half' has bee converted into a benzenoid derivative. Apoc chenine is, in fact, a quinolyldiethylphe

$$C_9H_6N : C_6H_2Et_2OH[Et : Et : OH=4 : 5 : 6$$

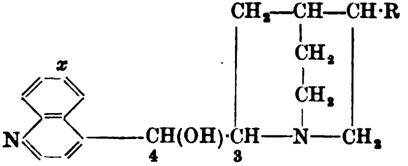
These and other reactions recall those of trop which has a dicylic nucleus with a nitroge atom, common to the two rings and all recent formulæ assigned to cinchonine quinine have represented the 'second half' the molecule by such a structure (*see* von Mil and Rohde, Ber. 1894, 27, 1187, 1279; 189 1056; 1900, 33, 3214; Königs, J. pr. Che 1900, [ii.] 61, 1; Annalen, 1906, 347, 143; Rab *ibid.* 1906, 350, 180; Ber. 1908, 41, 62; 1909, 364, 330; 1909, 365, 353, 366; 1910, 85). In determining the exact form of 'second half' the most important final fac have been as follows:—

1. When cinchonine is heated with ac acid it is converted into *cinchotoxine* (cinc cine), which is isomeric with cinchonine, behaves as a secondary base and con

carbonyl group. Cinchotoxine no longer possesses the characteristic physiological action of cinchonine, but is highly toxic. Quinine under similar conditions yields *quinotoxine*.

2. On careful oxidation with chromic acid in presence of acetic or sulphuric acid, cinchonine $C_{19}H_{22}ON_2$ furnishes a new base *cinchoninone* $C_{19}H_{20}ON_2$, which contains a carbonyl group, and on treatment with nitrous acid yields *cinchoninic* acid (p. 672), and an oxime which on hydrolysis yields *meroquinenine* (p. 672) and hydroxylamine. Cinchonidine also yields cinchoninone, whilst quinine and quinidine yield the same quininone (methoxycinchoninone) (Rabe, Ber. 1907, 40, 3655; 1908, 41, 62; Annalen, 1909, 365, 353; 1910, 373, 85; 1911, 382, 365).

On the basis of all these results Rabe has put forward the following general formula for this group of alkaloids—



The numbered carbon atoms are asymmetric.

In cinchonine, cinchonidine, quinine, and quinidine R=—CH : CH_2.

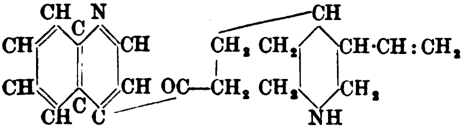
In hydrocinchonine, hydrocinchonidine, hydroquinine and hydroquinidine R=—$CH_2\cdot CH_3$ (*see* p. 674).

In cinchonine, cinchonidine, hydrocinchonine, and hydrocinchonidine *x*=H.

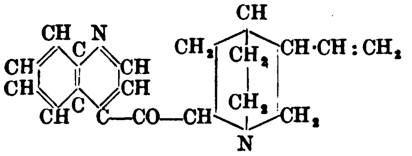
In quinine and quinidine and their hydrobases *x*=OMe.

In cupreine *x*=OH.

The following formulæ represent cinchotoxine and cinchoninone :—



Cinchotoxine (Rabe).



Cinchoninone (Rabe).

Miscellaneous cinchona alkaloids.

Cinchonamine $C_{19}H_{24}ON_2$ is contained in *Remijia Purdieana* (Wedd.). Crystals, m.p. 184°–185°. The salts are crystalline. The nitrate is remarkable in being nearly insoluble in dilute nitric acid (Arnaud, Bull. Soc. chim. 1884, [ii.] 41, 590; Hesse, Annalen, 1884, 225, 218).

Conquinamine $C_{19}H_{24}O_2N_2$. An isomeride of quinamine (p. 674), with which it occurs in several species of cinchona bark, especially in *C. succirubra* (Par.) (Hesse, Annalen, 1881, 209, 62; Oudemans, *ibid.* 1881, 209, 38).

Properties. Crystals, m.p. 121°. Very slightly soluble in water. Soluble in alcohol, chloroform, or ether. Dextrorotatory. The salts are crystalline and soluble in water.

Cupreine $C_{19}H_{22}O_2N_2$ is contained, with quinine, &c., in the bark of *Remijia pedunculata* (Flueck.), a plant closely related to, although distinct from, the cinchonas (Paul and Cownley, Pharm. J. 1884, [iii.] 15, 221, 401; Hesse, Annalen, 1885, 230, 57).

Preparation. The total alkaloids of cuprea bark are dissolved in dilute sulphuric acid, the solution is exactly neutralised, when the sulphates of cupreine and quinine crystallise out. These salts are dissolved in dilute sulphuric acid, and precipitated with excess of soda, which dissolves the cupreine and some of the quinine. On shaking the mixture with ether the quinine is dissolved by it, whilst the alkaline solution contains the cupreine. The aqueous liquid is now neutralised with dilute sulphuric acid when the cupreine sulphate crystallises out. The base is obtained by precipitating a solution of the recrystallised sulphate with ammonia. The precipitated alkaloid is crystallised from its solution in boiling ether and dried. It is then washed with chloroform and finally crystallised from alcohol (Hesse, *l.c.*).

Properties. Prisms with $2H_2O$, which lose their water at 120°, and then melt at 198°. Slightly soluble in ether or chloroform, more soluble in alcohol. Soluble in aqueous soda or potash; less soluble in aqueous ammonia; lævorotatory $[\alpha]_D = -175{\cdot}5°$ in dry alcohol. Ferric chloride produces a dark-green colour, and ammonia, after the addition of chlorine water, produces the green coloration known as the thalleioquin reaction (*see* p. 667).

Cupreine possesses both acid and basic properties. As a base it is diacidic. The neutral salts are crystalline solids; the acid salts are colourless, and their solutions are not fluorescent. Cupreine dissolves in aqueous alkalis and unites with bases to form definite compounds. One of these is of special interest, viz. that produced by the combination of cupreine with quinine, which may be effected by dissolving equimolecular proportions of quinine and cupreine in dilute sulphuric acid, precipitating with ammonia, and crystallising from ether. This compound

$$(C_{19}H_{22}O_2N_2\cdot C_{20}H_{22}O_2N_2,4H_2O)$$

was first obtained from the total alkaloids of cuprea bark, and was thought to be a single alkaloid 'homoquinine.' The substance melts at 177°, is lævorotatory, and dissolves with difficulty in ether, but readily in alcohol. It behaves as a single diacidic base and forms well-crystallised salts; the normal sulphate is fluorescent in acid solution. The compound may be resolved into its constituents by precipitating the sulphate with excess of soda, and extracting with ether, which dissolves some of the quinine. By repeating the process a number of times the two alkaloids may be more or less completely separated (Howard and Hodgkin, Chem. Soc. Trans. 1882, 41, 66; Hesse, Annalen, 1884, 225, 98; 1884, 226, 242; 1885, 230, 72; Paul and Cownley, *l.c.*).

For the methods of detecting cupreine in commercial quinine sulphate, *see Quinine* (p. 669). On methylation cupreine furnishes quinine, which is its methyl ether (for formula, *see* p. 673).

Hydrocinchonidine $C_{19}H_{24}ON_2$, also known as cinchamidine, obtained by Forst and Böhringer as a residue in the oxidation of commercial cinchonidine sulphate by permanganate (Ber. 1881, 14, 1270; 1882, 15, 520; Hesse, *ibid.* 1881, 14, 1683; Annalen, 1882, 214, 1). Hexagonal leaflets from dilute alcohol, m.p. 229°–230°, difficultly soluble in ether, attacked with difficulty by permanganate. For formula, *see* p. 673.

Hydrocinchonine $C_{19}H_{24}ON_2$, also known as 'cinchotine,' ψ-cinchonine, and cinchonifine, occurs in commercial cinchonine sulphate, from which it may be isolated by adding potassium iodide to a solution of the hydrochlorides when hydrocinchonine hydriodide is precipitated, or it may be obtained through the platinichloride, which is more soluble than that of cinchonine. Prisms, anhydrous, m.p. 277·3° (265°–267°, Forst and Böhringer, Ber. 1881, 14, 436; and von Arlt, Monatsh. 1899, 20, 425), $[\alpha]_D = +204{\cdot}5°$ ($+229{\cdot}6°$ Jungfleish and Léger, Compt. rend. 1901, 132, 410, 828) in alcohol. The salts crystallise well. The alkaloid is closely related to cinchonine in constitution (p. 673) (Hesse, Annalen, 1873, 166, 256; 1879, 197, 362; Königs and Horlein, Ber. 1894, 27, 2292; von Miller and Rohde, Ber. 1895, 28, 1063, 1075).

Hydroquinidine $C_{20}H_{26}O_2N_2$ occurs in the mother liquors from which quinidine sulphate has been crystallised and can be separated from quinidine by oxidising the latter with permanganate. Crystals with $2\frac{1}{2}H_2O$, m.p. 167°; readily soluble in alcohol, sparingly in ether. The sulphate $B,H_2SO_4,12H_2O$ fluoresces blue in dilute sulphuric acid and gives the thalleioquin reaction (p. 667). Like hydroquinine, hydroquinidine is not readily oxidised by permanganate (Forst and Böhringer, Ber. 1881, 14, 1954; 1882, 15, 520, 854; Hesse, *ibid.* 1882, 15, 3010; Annalen, 1888, 243, 146).

Hydroquinine $C_{20}H_{26}O_2N_2$ occurs in cinchona bark and is almost invariably present in small quantity in modern commercial quinine sulphate. It can be prepared from this latter source by recrystallising the quinine sulphate from water when the more soluble hydroquinine salt remains in the mother liquors, together with the sulphates of other cinchona alkaloids (p. 669). The mother liquors are then treated with permanganate solution until a permanent red tint is produced. From the filtrate hydroquinine can be recovered by adding alkali and shaking out with ether. It is precipitated by alkalis either in amorphous form or in a crystalline form (with $2H_2O$) depending on the conditions.

Properties. Needles from chloroform, m.p. 172°, lævorotatory, readily soluble in most organic solvents, sparingly in water. Like quinine it forms 3 series of salts; the neutral sulphate B_2,H_2SO_4, 6 or $8H_2O$; and the acid sulphate $B,H_2SO_4,3H_2O$ are crystalline, but the disulphate $B,2H_2SO_4$ is amorphous.

Reactions and constitution. Hydroquinine closely resembles quinine in reactions: it fluoresces blue in dilute sulphuric acid solution, gives the thalleioquin reaction (p. 667), and yields a compound analogous to 'herepathite' (p. 667), and possessing similar properties. It also forms addition products with various organic substances, including cupreine (p. 673). Unlike quinine, it is not readily oxidised by permanganate. Hydroquinine is closely related to quinine, but is isomeric, not identical with the dihydroquinine obtained by the reduction of quinine (Hesse, Ber. 1882, 15, 854; Annalen. 1887, 241, 255, 273, 279; Pum, Monatsh. 1895, 16, 72). For estimation of hydroquinine in commercial quinine sulphate, see p. 669.

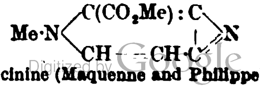
Quinamine $C_{19}H_{24}O_2N_2$. An alkaloid found by Hesse in *C. succirubra* (Pau.) bark, and in small quantity in many other cinchona barks, but notably in *C. Ledgeriana* (Hesse. Annalen, 1873, 166, 266; Ber. 1877, 10, 2157).

Preparation. The total alkaloids are dissolved in dilute sulphuric acid, and the solution neutralised with ammonia. The quinine and cinchonidine are removed by precipitating the liquid with a strong solution of Rochelle salt, and the filtrate is then precipitated with soda. The washed precipitate is extracted with ether, which dissolves the quinamine. The alkaloid thus obtained is purified by re-extracting it with dry ether and crystallising the ethereal residue from alcohol. The alkaloid is finally purified by conversion into the nitrate, which is re-crystallised from water, and the alkaloid regenerated from the pure salt (Hesse, *l.c.*; Oudemans, Annalen, 1879, 197, 50).

Properties. Long silky anhydrous needles; m.p. 172°. Slightly soluble in cold water; very soluble in boiling alcohol, ether, benzene or light petroleum. Dextrorotatory $[\alpha]_D = +93{\cdot}4°$ in chloroform. Quinamine is coloured yellow by warm sulphuric acid, and orange by nitric acid. The salts are crystalline, and soluble in water.

Rheadine $C_{21}H_{21}O_6N$. Colourless needles, m.p. 245°–247° (Pavesi). Occurs in red poppy, also in opium poppy, opium, and *P. hybridum* (Linn.). Not poisonous. On treatment with acids it is converted into *rheagenine*, m.p. 235° (Hesse, *ibid.* 1866, 140, 146; Pavesi, Chem. Soc. Abstr. 1906, 90 ii. 483). *Papaver dubium* (Linn.), according to Pavesi (Chem. Soc. Abstr. 1905, 88, [i.] 368; 1907, 92, [i.] 870), contains *aporeine* $C_{18}H_{16}O_2N$, amorphous; yielding crystalline salts. Aporeine exercises in frogs a tetanising action similar to that of thebaine.

Ricinine $C_8H_8O_2N_2$ occurs in castor seed and in young castor seedlings (*Ricinus communis* [Linn.]) along with the toxalbumin 'ricin.' Crystallises from water or alcohol in rectangular prisms or tablets, m.p. 201°, sublimes without decomposition, and is optically inactive. It is precipitated by mercuric chloride or iodine solution, but not by the other usual alkaloidal reagents (Tuson. Chem. Soc. Trans. 1864, 17, 195; Soave, Chem. Zentr. 1895, i. 853; Evans, J. Amer. Chem. Soc. 1900, 22, 39). On hydrolysis by alkalis it yields 1 mol. each of methyl alcohol and ricininic acid $C_7H_6O_2N_2$ (brilliant slender needles decomposing at 320°); the latter when heated with hydrochloric acid at 150° decomposes forming carbon dioxide, ammonia, and hydroxymethylpyridone hydrochloride, whence Maquenne and Philippe (Compt. rend. 1904, 138, 506; 138, 840) assign the following constitution to ricinine:



Ricinine (Maquenne and Philippe).

Rubijervine. *See Cevadine and the Veratrum alkaloids* (p. 644).

Sabadilline, Sabadine, and **Sabadinine.** *See Cevadine and the Veratrum alkaloids* (p. 644).

Sanguinarine $C_{20}H_{15}O_4N$ occurs in *Sanguinaria canadensis* (Linn.) and other papaveraceous plants (Fischer, Arch. Pharm. 1901, 239, 409, 421; and Schmidt, *ibid.* 395). It is a colourless, optically inactive, crystalline monacidic base, m.p. 212°, forming red crystalline salts (König, Chem. Soc. Abstr. 1891, i. 843). Exerts a narcotic action, but causes tetanus and excitement.

Scopolamine. *See* under *Atropine* (p. 639).

SENECIFOLINE AND THE ALKALOIDS OF SENECIO SPP.

Of the various species of *Senecio* only three have been examined so far, viz. *Senecio latifolius* (Banks and Soland.) of South Africa, *S. Jacobaea* (Linn.) (ragwort), and *S. vulgaris* (Linn.) (groundsel), which are cosmopolitan in distribution. The two first-named plants are poisonous and cause hepatic cirrhosis in cattle and horses in South Africa, Canada, and New Zealand (Bull. Imp. Inst. 1911, 9, 346).

Senecifoline $C_{18}H_{27}O_8N$ was isolated from *S. latifolius* (Banks and Soland.) by Watt (Chem. Soc. Trans. 1909, 95, 466). It crystallises in colourless, rhombic plates, m.p. 194°–195°, $[a]_D +28° 8'$ in alcohol, and is soluble in ether or chloroform, insoluble in water or light petroleum. The salts crystallise well and are lævorotatory. On hydrolysis by heating an aqueous solution of the sulphate with alkali the alkaloid furnishes *senecifolinine* $C_8H_{11}O_2N$ (which is very soluble in water and yields a hydrochloride crystallising in rhombic prisms, m.p. 168°, $[a]_D -12° 36'$) and *senecifolic acid* $C_{10}H_{16}O_6$, m.p. 198°–199°, $[a]_D +28° 22'$, crystallising in six-sided plates.

Senecifolidine $C_{18}H_{25}O_7N$ accompanies senecifoline in *S. latifolius* (Banks and Soland.). It forms rhombic plates, m.p. 212°, $[a]_D -13° 56'$ in alcohol. Salts crystalline.

Senecifoline and senecifolidine are both poisonous; when given in large doses they affect the central nervous system like convulsive poisons, and in smaller doses produce hæmorrhage, which may occur in any organ, but is constant in the liver and is nearly always present in the stomach and bowels. Extracts of *S. vulgaris* produce similar results (Cushny, Proc. Roy. Soc. 1911, B, 84, 188).

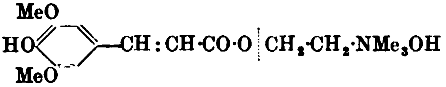
Senecionine $C_{18}H_{25}O_6N$ was isolated by Grandval and Lajoux from *Senecio vulgaris* (Linn.) (the common groundsel). It crystallises in rhombic plates, has $[a]_D -80{\cdot}49°$ in chloroform, furnishes amorphous salts, and is bitter. It is accompanied by *Senecine*, which yields a sparingly soluble acid tartrate (Compt. rend. 1895, 120, 1120). From Cushny's preliminary observations on *Senecio vulgaris* recorded above, the alkaloids of this plant would appear to resemble senecifoline and senecifolidine in physiological action.

Septentrionaline. *See* under *Aconitine* (p. 634).

Sinalbine $C_{30}H_{42}O_{15}N_2S_2$, first isolated by Will and Laubenheimer from white mustard seed (Annalen, 1879, 199, 162). Crystallises with $5H_2O$, m.p. 83°–84°; anhydrous, m.p. 139°. Lævorotatory (Gadamer, Apoth. Zeit. 1896, 11, 752; Arch. Pharm. 1897, 235, 44, 570). Sinalbine is one of a series of closely related glucosides from plants belonging to the *Cruciferæ*, *e.g.* sinigrin (potassium myronate), gluconasturtiin, and glucotropæolin, all of which on hydrolysis by enzymes furnish dextrose, a mustard oil (alkylthiocarbimide) and a third substance. In the case of sinalbine the third substance is the alkaloid *Sinapine* (*see* below), whilst in the three other glucosides mentioned it is potassium hydrogen sulphate. According to Gadamer (*l.c.*) sinalbine is hydrolysed into *p*-hydroxybenzylthiocarbimide, dextrose, and sinapine hydrogen sulphate, and has the following constitution, in which the dotted lines show the residues of the three components.

$$HO{\cdot}C_7H_6N:C(S \,\vdots\, C_6H_{11}O_5) \,\vdots\, O{\cdot}SO_2{\cdot}O{\cdot}NMe_3{\cdot}CH_2 {\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH:CH{\cdot}C_6H_2(OH)(OMe)_2.$$

Sinapine $C_{16}H_{25}O_6N$ occurs in white mustard seed from which it may be isolated by extraction with alcohol and precipitation as the thiocyanate, m.p. 176°, which is stable, though the alkaloid itself is so unstable that it cannot be kept in the free state. It is an ester of choline and sinapic acid, and, according to Gadamer, has the following constitution—



Sinapic acid residue. Choline residue.

Sinapine.

The acid sulphate $B{\cdot}H_2SO_4,3H_2O$ forms rectangular leaflets, m.p. 127°. The chief papers relating to this alkaloid are as follows: von Babo and Hirschmann, Annalen, 1852, 84, 10; Will and Laubenheimer, *ibid.* 1879, 199, 162; Remsen and Cole, J. Amer. Chem. 1884, 6, 52; and Gadamer, Arch. Pharm. 1897, 235, 44, 570; Apoth. Zeit. 1896, 11, 752).

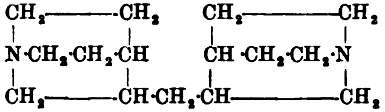
Solanine. This name was first applied by Desfosses (B. J. 1820, 2, 114) to a base isolated from *Solanum nigrum* (Linn.), and subsequently from *Solanum Dulcamara* (Linn.), and, later on, from other *solanaceous* plants, including potato and tomato plants. The composition and the homogeneity of solanine from different sources have not yet been ascertained beyond doubt, but it seems likely, as Firbas has stated (Monatsh. 1889, 10, 541), that at least two substances of this type are present in these various plants, viz. *solanine* and *solaneine*, and these may be accompanied by *solanidine*, a basic decomposition product of solanine. All authorities are agreed that solanine is an alkaloidal glucoside, but there is good reason to believe that the substances from different plants that have been named solanine are not all identical. The principal recent papers relating to solanine and the related substances are Cazeneuve and Breteau, Compt. rend. 1899, 128, 887; Schulz, Zeit. Zuck-Ind. Böhm. 1900, 25, 89; Sage, Pharm. J. 1902, [iv.] 14, 174; Davis, *ibid.* 1902, [iv.] 15, 160; Oddo and collaborators, Gazz. chim. ital. 1905, 35, i. 27; 1906, 36, i. 310; 1911, 41, i. 490; Atti. R. Accad. Lincei. 1906, [v.] 15, ii. 312; 1907, [v.] 16, ii. 683; Wittmann (Monatsh. 1905, 26, 445; Romeo, Gazz. chim. ital. 1905, 35, ii.

579. Oddo deals chiefly with solanine-S $(C_{27}H_{46}O_9N)_2H_2O$, m.p. 275°–280°, from *Solanum sodomæum* tubers, which he regards as distinct from potato-solanine $C_{32}H_{51}O_{11}N$, m.p. 262°.

Sparteine $C_{15}H_{26}N_2$, a liquid alkaloid obtained from broom (*Cytisus scoparius* (Link.) or *Spartium scoparium* [Linn.]) (Stenhouse, Annalen, 1851, 78, 15; Mills, *ibid.* 1863, 125, 71); subsequently shown to be identical with lupinidine from yellow lupin seeds (*L. luteus*) by Willstätter and Marx (Ber. 1904, 37, 2351). It may be obtained from broom tops by extraction with very dilute sulphuric acid, concentration of the extract and steam-distillation of the residue, after addition of alkali. The crude alkaloid may be purified by distillation in a current of hydrogen.

Properties. A colourless liquid, sp.gr. 1·034 at 0°, b.p. 188° under 18·5 mm., or 325° in a current of hydrogen under 754 mm. pressure (Moureu and Valeur, Compt. rend. 1903, 137, 194), 180·5° under 18 mm. (W. and M. *l.c.*). Slightly soluble in water, soluble in alcohol, ether, or chloroform; insoluble in light petroleum or benzene. The aqueous solution is alkaline and very bitter. $[\alpha]_D = -14{\cdot}6°$ in alcohol (Bamberger, Annalen, 1886, 235, 368), $-16{\cdot}42°$ (M. and V. *l.c.*) at 20°. Sparteine is a diacidic base, which forms difficultly crystallisable salts. The alkaloid and its salts are toxic. *V.* also p. 101.

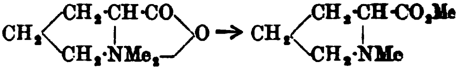
Reactions and constitution. Sparteine behaves towards alkyl iodides as a ditertiary diamine but contains no methyl linked to N (Herzig and Meyer, Monatsh. 1894, 15, 613; 1895, 16, 599; M. and V. *l.c.*). It furnishes no reduction products, and is unaffected by permanganate. Sparteine reacts with methyl iodide to form two monomethiodides, which are regarded as stereoisomerides. On 'exhaustive methylation' sparteine furnishes hemisparteilene $C_{15}H_{23}N$ and trimethylamine and finally sparteilene $C_{15}H_{20}$. On oxidation with chromic acid it yields spartyrine $C_{15}H_{24}N_2$, and eventually oxysparteine $C_{15}H_{24}ON_2$. From these and other data Moureu and Valeur (Compt. rend. 1905, 141, 261, 328) have assigned the following formula to sparteine—



Sparteine.

The principal papers relating to sparteine are as follows: Ahrens, Ber. 1887, 20, 2218; 1888, 21, 825; 1891, 24, 1095; 1892, 25, 3607; 1893, 26, 3035; 1897, 30, 195; Moureu and Valeur, Compt. rend. 1903, 137, 194; 1905, 140, 1601, 1645; 141, 49, 117, 261, 328; 1907, 145, 815, 929, 1184, 1343; 1908, 146, 79; 1911, 152, 386, 527; 1912, 154, 309; Bull. Soc. chim. 1909, [iv.] 5, 31, 37, 40; Wackernagel and Wolffenstein, Ber. 1904, 37, 3238; Willstätter and collaborators, *ibid.* 1904, 37, 2351; 1905, 38, 1772.

Stachydrine $C_7H_{13}O_2N$ occurs with glutamine, tyrosine and other amino acids in the tubers of *Stachys tuberifera* (von Planta and Schulze, Ber. 1890, 23, 1699; 1893, 26, 939); and in orange leaves (Jahns, *ibid.* 1896, 29, 2065); Schulze and Trier, Zeitsch. physiol. Chem. 1910, 67, 59). It crystallises from alcohol, on adding ether, in hygroscopic crystals with $1H_2O$ m.p. 210° (dry) and yields crystalline salts; aurichloride $B{\cdot}HCl{\cdot}AuCl_3$ rhombic leaflets, m.p. 225°. The base is neutral and optically inactive. Schulze and Trier (*ibid.* 1909, 59, 233) have assigned to it the following formula—



Stachydrine (Schulze and Trier). Methyl hygrinate.

which receives support from its conversion into methyl hygrinate on distillation (Trier, *l.c.* 1910, 67, 324), and its synthesis by treating ethyl hygrinate methiodide with silver oxide (S. and T. Ber. 1909, 42, 4654; *cf.* Engeland Arch. Pharm. 1909, 247, 463). *See* also p. 149.

Staphisagroine and **Staphisagroidine.** *See* under *Delphinine* (p. 651).

STRYCHNINE AND THE STRYCHNOS ALKALOIDS (*see* also NUX VOMICA, vol. iii. p. 719).

Strychnine $C_{21}H_{22}O_2N_2$, the principal alkaloid of *Strychnos Nux-vomica* (Linn.), *S. Ignatii* (Berg.), *S. colubrina* (Linn.), *S. Tieuté* (Lesch.), and other *Strychnos* spp. The nearly allied alkaloid brucine usually occurs with strychnine in these plants, but *S. Rheedei* contains brucine only. The seeds of the first two alone are used as sources of strychnine. Strychnine was discovered by Pelletier and Caventou in 1817. The seeds of *S. Nux-vomica* vary in the amount of total alkaloid (strychnine and brucine) they contain. As little as 1 p.c. has been found, and as much as 5 p.c. in the seeds of the Ceylon nux-vomica. About one-third of the total alkaloid is strychnine and two-thirds brucine (Dunstan and Short, *ibid.* 1882–1883, [iii.] 13, 1053; 1884–1885, 15, 1). The total alkaloids from the seeds of *S. Ignatii* are richer in strychnine than those of *S. Nux-vomica*. The leaves of *S. Nux-vomica* contain *strychnicine*, needles, m.p. 240° (van Boorsma, Bull. Inst. bot. Buit. 1902, 14, 3).

Preparation. The following process may be used for the extraction of strychnine and brucine from the seeds of *S. Nux-vomica* or *S. Ignatii* (*see* also NUX VOMICA). The finely-powdered seeds are made into a paste with water and one-fourth of their weight of slaked lime. The mixture is thoroughly dried on the water-bath and the dry mass finely powdered. The alkaloids are now dissolved from it by hot percolation with a suitable solvent (amyl alcohol, benzene, or chloroform) in an extraction apparatus. The solvent is shaken with dilute sulphuric acid, which removes the alkaloids as sulphates. These salts may be crystallised from the neutral solution, or the alkaloids may be regenerated, and the mixture (strychnine and brucine) extracted with dilute (25 p.c.) alcohol, which dissolves the brucine, and leaves nearly the whole of the strychnine undissolved. It is purified by recrystallisation from alcohol.

Properties. Rhombic prisms, m.p. 268° (Loebisch and Schoop, Monatsh. 1885, 6, 858). At higher temperatures some of the alkaloid sublimes unchanged. According to Loebisch (*l.c.*), the alkaloid distils without decomposition at 270° under 5 mm. pressure. Lævorotatory, $[\alpha]_D$ −36° in neutral salts (Tykociner, Rec. trav. chim. 1882, 1, 46). Very slightly soluble in water (1 in 6667, at 15°; 1 in 2500 at 100°). The aqueous solution is alkaline, and even when largely diluted, has a persistent bitter taste; the bitterness is perceptible in a solution containing 1 part of strychnine in 700,000 parts of water. The alkaloid is sparingly soluble in absolute alcohol (0·302 in 100 at 8·25°), ether (1 in 5500 at 25°), but is dissolved by chloroform (1 in 6), benzene (1 in 150 at 25°), amyl alcohol (1 in 180 at 25°), or 90 p.c. alcohol (1 in 170).

Strychnine is a violent poison, giving rise to tetanic spasms, owing to the greatly increased excitability of the spinal cord. Half a grain of the alkaloid has proved fatal to man.

Strychnine is a monacidic base: its salts are, as a rule, crystalline and soluble in water. The hydrochloride $B{\cdot}HCl,2H_2O$ forms small colourless prisms, and is soluble in 35 parts of cold water; the nitrate $B{\cdot}HNO_3$ forms colourless, glancing prisms, and is soluble in 80 parts of water at 18°–19°; the sulphate $B_2{\cdot}H_2SO_4,5H_2O$ forms colourless prisms, soluble in 31 parts of water at 25°. All the salts are neutral in aqueous solution.

Reactions and Detection. Strychnine, which is one of the most stable of alkaloids, is not coloured by sulphuric acid, and gives at most only a yellow coloration with nitric acid. It may be heated to 100° with sulphuric acid without being appreciably affected. When brought into contact with certain oxidising agents it exhibits a striking colour reaction, which is generally relied on for its detection. If the alkaloid is dissolved in a drop of strong sulphuric acid, and a small piece of potassium dichromate, manganese dioxide, ceric oxide, or potassium permanganate is stirred into the mixture, a play of colours is observed, beginning with blue, which gradually passes through violet and red to yellow (Marchand, J. Pharm. Chim. [iii.] 4, 200). The only other alkaloids which behave exactly like strychnine in this respect are curarine and gelsemine. Several alkaloids, however, give a somewhat similar colour reaction, but most of these are coloured by sulphuric acid alone, and may thus be readily distinguished from strychnine. The presence of foreign organic compounds frequently obscures the colour, and the alkaloid to be tested must, therefore, first be isolated in a nearly pure state, and separated, as far as possible, from any other alkaloid that may be present. This colour reaction cannot be obtained in the presence of much brucine, the alkaloid which accompanies strychnine in the plant, since it gives a deep-red coloration when oxidised which obscures the play of colours produced by the strychnine. This alkaloid may, however, be removed by oxidation with dilute nitric acid, the strychnine being recovered from the acid liquid by adding ammonia and extracting with chloroform (Shenstone, Pharm. J. 1877–1878, [iii.] 8, 445; Hanriot, Compt. rend. 1883, 97, 267), or the mixed alkaloids may be washed with chlorine water, when the brucine is converted into the soluble dichlorobrucine, which dissolves, leaving a residue of strychnine (Beckurts, Arch. Pharm. 1890, 228, 326). In toxicology, where traces of impurity in the alkaloidal residue would give rise to darkening when the sulphuric acid is added, the residue may be moistened with the strong acid and heated on the water-bath until the impurity is completely decomposed; water is then added, and the strychnine recovered by adding ammonia and extracting with chloroform.

Estimation of total alkaloids. For the estimation of the total alkaloids in nux vomica, Ignatius beans, &c., and in the medicinal preparations made from these plants the following processes have been devised.

For the seeds of *S. Nux-vomica* or *S. Ignatii* 5 grms. of the seeds dried at 100°, and finely ground, are exhausted of alkaloidal salts by hot percolation in an extraction apparatus with chloroform, to which has been added 25 p.c. by volume of alcohol. The solution is mixed with about half its volume of dilute sulphuric acid (5 p.c.) and well shaken. The mixture separates into two layers, the alkaloids being in the upper aqueous layer and the colouring matter, &c., in the lower layer of chloroform. When the alkaloidal salts have been completely removed from the chloroform by a repetition of this process, the solution of the acid sulphates of strychnine and brucine is made alkaline with ammonia, and extracted with chloroform until the alkaloids are removed. The alkaloidal residue left by the evaporation of the chloroform is dried at 100° and weighed (Dunstan and Short, Pharm. J. 1882–1883, [iii.] 13, 665, 1053).

For the tincture of nux vomica 50 c.c. of the tincture are evaporated almost to dryness on the water-bath. The residue is dissolved in dilute sulphuric acid, and to the clear acid liquid, ammonia is added in excess, and the alkaloid removed by shaking with chloroform. The residue of alkaloid left by the evaporation of the chloroform is dried at 100° and weighed (Dunstan and Short, Pharm. J. 1883–1884, [iii.] 14, 292).

For the liquid extract of nux vomica, 10 c.c. is evaporated nearly to dryness at 100° and dissolved in about 50 c.c. of 5 p.c. aqueous sodium carbonate, and the liquid twice extracted with half its volume of chloroform. The solution of the alkaloid in chloroform is shaken with half its volume of dilute sulphuric acid, and the chloroform, which contains fat and resin, removed. The clear acid liquid is made alkaline with ammonia, and the alkaloid extracted with chloroform. The solution of the alkaloids in chloroform is evaporated, dried at 100°, and weighed (Dunstan and Short, Pharm. J. 1883–1884, [iii.] 14, 621).

Estimation of strychnine. The alkaloid obtained by all these processes is a mixture of strychnine and brucine. The two alkaloids possess very similar properties, and are not easy to separate. On the large scale an approximate separation may be effected by extracting the residue with dilute alcohol (25 p.c. by volume), which readily dissolves the brucine but only traces of the strychnine.

For quantitative purposes advantage may be taken of the great difference in the solubilities of the ferrocyanides of strychnine and brucine; the strychnine salt, being very slightly soluble in water, separates from dilute acidified solutions as a characteristic granular precipitate, whilst the brucine ferrocyanide, being readily soluble in water, does not separate except from concentrated solutions. When both alkaloids are present the separation is not quite so sharp as might be anticipated, but it has been proved that sufficiently accurate results for ordinary analytical purposes may be obtained, if the following directions are adhered to (Dunstan and Short, Pharm. J. 1883–1884, [iii.] 14, 621; *cf.* Carr and Wright, *ibid.* 1900, [iv.] 11, 82). Any quantity less than 0·2 grm. of the mixed alkaloids (the British Pharmacopœia, 1898, uses the total alkaloid from 10 c.c. of the liquid extract or from 100 c.c. of the tincture of nux-vomica) is dissolved in about 10 c.c. of dilute sulphuric acid (5 p.c. by volume). The solution is diluted with water to about 175 c.c., and finally made up to 200 c.c. with 5 p.c. aqueous potassium ferrocyanide. The liquid is stirred occasionally, and allowed to stand for about 6 hours, by which time the strychnine ferrocyanide will have separated as a white granular precipitate. The precipitate is collected and washed with water just acidified with sulphuric acid until the washings are scarcely bitter. Since strychnine ferrocyanide is difficult to dry without decomposition, the moist salt is decomposed by the addition of ammonia solution, in which it is completely soluble. The alkaline liquid is twice extracted with chloroform, which removes the strychnine. The solution in chloroform is evaporated on the water-bath to a small volume, the remainder of the chloroform spontaneously evaporated, and the residue finally dried in a covered dish (to avoid loss by spurting) and weighed. The brucine may be estimated by difference, or it may be dissolved from the filtrate and washings, made alkaline with ammonia, by shaking with chloroform, separating, evaporating, and weighing in the usual manner. The British Pharmacopœia, 1898, requires that tincture of nux-vomica and liquid extract of nux-vomica shall contain 0·24 to 0·26 grm. and 1·5 grms. of strychnine in 100 c.c., respectively, when assayed by the above process.

Beckürts and Holst (Arch. Pharm. 1887, [iii.] 25, 313) have proposed to apply this method volumetrically.

A method of separation depending on the greater solubility of brucine picrate has also been proposed (Gerock, *ibid.* 1889, [iii.] 27, 158). Keller has suggested a method for the estimation of strychnine in presence of brucine depending on the readiness with which the latter alkaloid can be destroyed by dilute nitric acid, and modifications of this have been advocated by Stoeder (Ned. Tijd. Ph. 1899, 11, 1), Gordin (Arch. Pharm. 1902, 240, 641), Howard (Analyst, 1905, 30, 261), and Reynolds and Sutcliffe (J. Soc. Chem. Ind. 1906, 25, 512).

Brucine $C_{23}H_{26}O_4N_2$. This alkaloid occurs with strychnine in *S. Nux-vomica* (Linn.) and in other species of *Strychnos*. In the seeds of *S. Nux-vomica* about two-thirds of the total alkaloid is brucine (Dunstan and Short, Pharm. J. 1884–1885, [iii.] 15, 1). In the seeds of *S. Ignatii* the proportion of brucine appears to be smaller.

Preparation. The total alkaloid having been extracted from the plant by the method described for strychnine, the mixture is repeatedly washed with dilute alcohol (25 p.c. by volume) and the brucine crystallised from the solution, and recrystallised several times from the same solvent or from water, the fractions which crystallise latest being almost, if not quite, pure brucine.

According to Flückiger (Pharm. Chem.), if the mixture of the two alkaloids is converted into the acetates and the solution is evaporated to dryness on the water-bath the strychnine acetate undergoes dissociation into the alkaloid and acetic acid, which volatilises. The brucine acetate remains unchanged, and may be dissolved from the residue by cold water and crystallised. For another method which is said to furnish quite pure brucine, *see* Shenstone, Chem. Soc. Trans. 1881, 39, 453; and also Nux-Vomica, vol. iii. p. 719.

Properties. Brucine separates from its solutions in water or aqueous alcohol in monoclinic prisms containing $4H_2O$, m.p. 105°, or with $2H_2O$ from alcohol (Moufang and Tafel, Annalen, 1899, 304, 24). The crystals lose their water at 100°, or on standing over sulphuric acid. The anhydrous substance melts at 178° (Claus, Ber. 1881, 14, 773); lævorotatory, $[\alpha]_D =$ in alcohol −85°, in chloroform −119° to 127° (Oudemans, Annalen, 1873, 166, 69). Slightly soluble in cold water (1 in 320), twice as soluble in boiling water, very soluble in alcohol, chloroform, or amyl alcohol; insoluble in ether. Brucine and its salts are bitter, and when subcutaneously injected in animals produce a physiological action resembling in kind that of strychnine, but much feebler. When administered internally to animals it produces little or no effect, owing chiefly to the rapidity with which it is eliminated (Brunton, Chem. Soc. Trans. 1885, 47, 143).

Brucine is a monacidic tertiary base; the ordinary salts are crystalline, and readily dissolve in water.

Reactions. Brucine is readily distinguished from strychnine, since it does not give rise to the characteristic play of colours when oxidised with chromic acid, &c., only an intense red coloration being produced, whilst brucine is further differentiated from strychnine by giving a deep-red coloration when mixed with nitric acid; this is a very delicate test for brucine, and conversely for nitric acid. This red coloration of brucine is distinguished from that produced when some other alkaloids (*e.g.* morphine) are mixed with nitric acid, by the action of stannous chloride or certain other reducing agents, which when cautiously added change the red coloration to violet.

When heated with strong hydrochloric acid brucine evolves two molecular proportions of methyl chloride (Shenstone, Chem. Soc. Trans. 1883, 43, 101; Hanssen, Ber. 1884, 17, 226).

Detection and estimation. Brucine may be detected by means of the properties and reactions described above. It may be estimated in plants and in medicinal preparations by the methods described in connection with strychnine (p. 677).

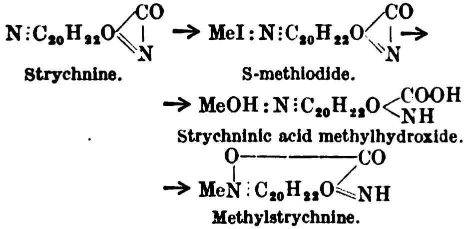
Constitution of strychnine and brucine. In spite of the fact that these two alkaloids were isolated nearly a century ago it is only quite recently that it has been possible to put forward constitutional formulæ for them. The principal facts so far ascertained in the chemistry of these alkaloids, and which bear directly on the problem of their constitution, are as follows:—

Both alkaloids contain two atoms of nitrogen, but behave as tertiary monacidic bases and contain no methyl linked to nitrogen. On treatment with alkalis they each take up 1 mo of water and form *strychninic* and *brucinic acids* respectively.

Brucine differs from strychnine by $(\cdot OCH_2)_2$, and in yielding 2 mols. of methyl iodide or methyl chloride when heated with concentrated hydriodic or hydrochloric acid. Apart from this the reactions of brucine are exactly parallel with those of strychnine, and the whole series of brucine derivatives correspond with those of strychnine and show a constant difference $(\cdot OCH_2)_2$.

These facts warrant the following assumptions: (1) of the two nitrogen atoms one is present as an imino group: N·CO, and this is converted into: NH·COOH in the transformation of strychnine $N{:}C_{20}H_{22}O\!<\!\begin{array}{l}CO\\ |\\ N\end{array}$ into strychninic acid $N{:}C_{20}H_{22}O\!<\!\begin{array}{l}CO_2H,\\ NH\end{array}$ and of brucine into brucinic acid. The N- atom concerned in the change is devoid of basic properties, and consequently the alkaloids are monacidic, this property depending on the second nitrogen atom. (2) Since the second nitrogen atom is tertiary, and yet has no methyl group attached, it must be linked up with a third carbon atom in a ring. (3) Brucine is probably a dimethoxy-derivative of strychnine.

On treatment with methyl iodide strychnine forms a methiodide, which, when warmed with barium hydroxide, forms methylstrychnine, which behaves as a betaine and is a secondary base; thus it furnishes a nitrosoamine and reacts with methyl iodide to form dimethylstrychnine, a substance which closely resembles N-methyltetrahydroquinoline in its properties, whence it may be concluded that strychnine contains a reduced quinoline nucleus. These changes may be represented thus—



$$N{:}C_{20}H_{22}O\!<\!\begin{array}{l}CO\\ |\\ N\end{array} \rightarrow MeI{:}N{:}C_{20}H_{22}O\!<\!\begin{array}{l}CO\\ |\\ N\end{array} \rightarrow$$

Strychnine. S-methiodide.

$$\rightarrow MeOH{:}N{:}C_{20}H_{22}O\!<\!\begin{array}{l}COOH\\ NH\end{array}$$

Strychninic acid methylhydroxide.

$$\rightarrow \begin{array}{l}O\text{———————}CO\\ |\\ MeN{:}C_{20}H_{22}O\!<\!NH\end{array}$$

Methylstrychnine.

The conclusion that strychnine contains a quinoline nucleus receives confirmation from the fact that the alkaloid is readily nitrated and sulphonated, and that on treatment with nitric acid it yields dinitrostrycholcarboxylic acid, which by loss of CO_2 passes into dinitrostrychol, which appears to be a dinitrodihydroxyquinoline $(NO_2)_2C_9H_3N(OH)_2$.

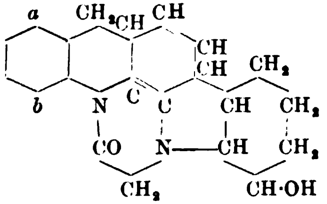
The study of the oxidation products of strychnine and brucine has also afforded useful data. When either alkaloid is oxidised with chromic acid it furnishes an acid

$$C_{15}H_{17}O_2N_2(COOH),$$

which contains no methoxyl, so that in the formation of this acid it must be the portion of the molecule containing the two $\cdot OCH_3$ groups of brucine that has been destroyed thus—

$C_{15}H_{17}O_2N_2\cdot C_6H_5$ Strychnine. $C_{15}H_{17}O_2N_2\cdot C_6H_3(OMe)_2$ Brucine.

The yield of this acid is unfortunately small, but on distillation with zinc-dust it yields diphenylimide (carbazole), a substance which also occurs among the products of the destructive distillation of strychnine. On the basis of these results Perkin and Robinson have suggested that strychnine and brucine must contain both a quinoline and a carbazole nucleus (Chem. Soc. Trans. 1910, 97, 305), and have suggested the following formula for strychnine—



Strychnine (Perkin and Robinson).

The formula for brucine differs from this only in having methoxyl groups substituted at positions *a* and *b*.

The principal papers relating to the chemistry of strychnine and brucine are as follows: Gerhardt, Annalen, 1842, 44, 279; Compt. rend. 1844, 19, 1105; Nicholson and Abel, Chem. Soc. Trans. 1850, 2, 241; Schützenberger, J. 1858, 373; Stahlschmidt, *ibid.* 1859, 395; Gal and Etard, *ibid.* 1878, 910; 1879, 820; Bull. Soc. chim. 1879, [ii.] 31, 98; Schiff, J. 1878, 910; Claus and collaborators, Ber. 1881, 14, 766, 774; Shenstone, Chem. Soc. Trans. 1881, 39, 456; 1883, 43, 101; 1885, 47, 139; Oechsner de Coninck, Compt. rend. 1882, 95, 298; 1884, 99, 1077; Hanriot, *ibid.* 1883, 96, 1671; Bull. Soc. chim. 1884, [ii.] 41, 235; Plugge, Ber. 1883, 16, 2683; Hanssen, *ibid.* 1884, 17, 2266, 2849; 1885, 18, 293, 777, 1917; 1886, 19, 521; 1887, 20, 451; Loebisch and Schoop, Monatsh. 1885, 6, 855; 1886, 7, 75, 609; 1888, 9, 629; Stoehr, Ber. 1885, 18, 3429; 1887, 20, 810, 1108, 2727; J. pr. Chem. 1890, [ii.] 42, 405; Tafel, Ber. 1890, 23, 2734; 1892, 25, 412; 1893, 26, 333; 1900, 33, 2216; Annalen, 1891, 264, 33; 1892, 268, 229; 1898, 301, 285; with Moufang, 1899, 304, 26; with Naumann, Ber. 1901, 34, 3291; Leuchs and collaborators, *ibid.* 1908, 41, 1711, 4393; 1909, 42, 770, 2494, 2681, 3067, 3703; 1910, 43, 1042, 2362, 2417; 1911, 44, 2136, 3040; 1912, 45, 201; Perkin and Robinson, Chem. Soc. Trans. 1910, 97, 305 (this paper gives a résumé of the principal facts bearing on the constitution of strychnine and brucine); Pictet and collaborators, Ber. 1905, 38, 2782, 2787; 1907, 40, 1172.

Taxine $C_{37}H_{52}O_{10}N$, an amorphous alkaloid contained in the seeds and leaves of the yew (*Taxus baccata* [Linn.]), m.p. 80°–82°. Almost insoluble in water; soluble in alcohol, ether, or chloroform. A monacidic base forming amorphous salts. A brown to purplish-blue coloration is produced when the alkaloid is dissolved in concentrated sulphuric acid (Marmé, Med. Cent. 1876, 14, 97; Bull. Soc. chim. 1876, [ii.] 26, 417; Hilger and Brande, Ber. 1890, 23, 464; Thorpe and Stubbs, Chem. Soc. Trans. 1902, 81, 874; Moss, Sci. Proc. Roy. Dubl. Soc. 1909, 12, 92). Taxine is a narcotic poison causing depression of the action of the heart and interference with respiration. *V.* also p. 420.

Thebaine. *See* under *Morphine* (p. 659).

Theobromine and **Theophylline.** *See* under *Caffeine* (pp. 641, 642).

Trigonelline $C_7H_7O_2N$ (*see Caffearine*, p. 640), an alkaloid existing in fenugreek, the powdered seeds of *Trigonella Foenum-graecum* [Linn.] (Jahns, Ber. 1885, 18, 2521; 1887, 20, 2840), various leguminous plants (Schulze and Frankfurt, *ibid.* 1894, 27, 769), in strophanthus seeds (Thoms, *ibid.* 1898, 31, 271, 404), and in coffee (Gorter, Annalen, 1910, 372, 337).

Properties. Prismatic crystals, with $1H_2O$, m.p. 130°; 218° (dry). Very soluble in water, slightly soluble in cold alcohol; very slightly soluble in ether, chloroform, or benzene. When heated with concentrated hydrochloric acid it yields methyl chloride and nicotinic acid (pyridine-β-carboxylic acid).

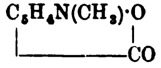
Jahns has proved that trigonelline is identical with the methylbetaine of nicotinic acid first prepared by Hantzsch (Ber. 1886, 19, 31; Jahns, 1887, 20, 2840). Nicotinic acid

$$(C_5H_4N{\cdot}COOH)$$

is heated with potash and methyl iodide, when methyl nicotinatemethiodide

$$C_5H_4N(CH_3I)CO{\cdot}OCH_3$$

is formed. On decomposition with silver oxide, this compound furnishes the betaine



$$\begin{array}{l}C_5H_4N(CH_3){\cdot}O\\ \quad|\qquad\qquad|\\ \quad\rule{0pt}{0pt}\text{—————}CO\end{array}$$

which is identical with trigonelline. The latter is also produced in the oxidation of nicotine methylhydroxide (Pictet and Genequand, Ber. 1897, 30, 2122). *V.* also p. 529.

Tropacocaine. *See* under *Cocaine* (p. 647).

Truxillines. *See* under *Cocaine* (p. 647).

Ulexine $C_{11}H_{14}ON_2$, found in *Ulex europæus* (L.) (Gerrard, Pharm. J. 1886–1887, [iii.] 17, 101, 229), is identical with cytisine from laburnum (p. 651).

Veratridine and **Veratrine.** *See Cevadine* (p. 644).

Vernine. *See* under *Caffeine* (p. 642).

Vicine $C_{20}H_{36}O_{15}N_8$, obtained by Ritthausen from *Vicia* spp. (J. pr. Chem. 1870, [ii.] 1, 336; 1873, [ii.] 7, 374; 1881, [ii.] 24, 202). Needles with $2H_2O$, m.p. 180° anhydrous (decomp.). Weakly basic. Undergoes hydrolysis by acids, yielding dextrose (?) (R. *l.c.*; 1899, [ii.] 59, 482), and *divicine* $C_8H_{14}O_4N_8$, which is readily oxidised by nitric acid to allantoin (?). *Convicine* $C_{20}H_{28}O_{16}N_6,2H_2O$ occurs with vicine (*l.c.*); rhombic leaflets. On hydrolysis it yields alloxantin, ammonia and a hexose (Ritthausen, *l.c.*; Schulze and Trier, Zeitsh. Physiol. Chem. 1910, 70, 143).

Xanthaline. *See* under *Papaverine* (p. 661).

Xanthine. *See* under *Caffeine, Theobromine, and the alkaloids of tea, cocoa, and coffee* (p. 642).

Yohimbine $C_{22}H_{30}O_4N_2$ or $C_{21}H_{26}O_3N_2$ occurs with *yohimbenine* $C_{35}H_{45}O_6N_3$ (crystalline, m.p. 135°), and possibly two other alkaloids in yohimbehe bark (*Corynanthe Yohimbi*) obtained from Kamerun (Spiegel, Chem. Zeit. 1896, 20, 970; 1897, 21, 833; 1899, 23, 59, 81; Ber. 1904, 37, 1759; Thoms, Chem. Soc. Abstr. 1898, 74, i. 455; Siedler, Chem. Zentr. 1902, ii. 1215). It crystallises in needles, m.p. 234°, $[a]_D +50{\cdot}9°$ in alcohol, forms a colourless solution with sulphuric acid, which becomes violet and then green when a crystal of potassium dichromate is stirred in it. Yohimbine is a monacidic, tertiary base, contains one methoxyl group, and probably one hydroxyl group. On heating at 120°–130° it loses $1H_2O$, forming an anhydrobase $C_{22}H_{28}O_3N_2$, and it is this base, not yohimbine itself, which forms salts. When heated with alcoholic potash, yohimbine is converted into noryohimbine (yohimboaic acid) $C_{20}H_{26}O_4N_2$, prisms, m.p. 257°–260°, and this on treatment with excess of diazomethane is reconverted into yohimbine (Spiegel, Ber. 1903, 36, 169; 1904, 37, 1759; 1905, 38, 2825; *cf.* Winzheimer, Ber. Pharm. Ges. 1902, 12, 391). The alternative formula $C_{21}H_{26}O_3N_2$ has been suggested by Fourneau and Fiore (Bull. Soc. chim. 1911, [iv.] 9, 1037) for yohimbine. Yohimbine produces local anæsthesia, and taken internally acts as an aphrodisiac; it is highly toxic. The chief papers relating to its physiological action are: Oberwarth (Virchow's Archiv. 1898, 153, 292); Gunn (Chem. Soc. Abstr. 1908, 94, i. 412); Tait (*ibid.* 1910, 98, ii. 434); Waller (*ibid.* 1911, 100, ii. 138).
W. R. D. and T. A. H.

VELOCITY OF REACTION *v.* CHEMICAL AFFINITY.

VENTILAGO MADERASPATANA (Gaertn.) is a large climbing shrub belonging to the order *Rhamnaceæ*, the root bark of which furnishes a dyestuff much valued in Southern India. It is very common in the Western Peninsula from the Konkan southwards, as well as in Ceylon and Burma, and, according to Lostard, it is largely collected in Mysore at certain periods of the year and exported to other districts of India.

The following are a few of its vernacular names: pitti (*Hindi*); raktapita (*Bengali*); pappili-chakka, surralpattai (*Tamil*); poplichukai (*Kan*); lokandi, kanwail (*Bomb*).

The root bark appears as dark purplish-brown scales, ribbons, or filaments, the dust from which, when it is ground to powder, irritates the throat in a marked manner. When treated with boiling water or alcohol it gives a red solution, which on addition of caustic alkali, changes to a deep crimson.

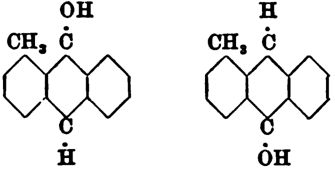
Perkin and Hummel (Chem. Soc. Trans. 1894, 65, 923), who examined this dyestuff, extracted the root bark with carbon disulphide, and obtained in this manner a resinous colouring matter *ventilagin*, together with the crystalline non-tinctorial substances described below.

Ventilagin $C_{15}H_{14}O_6$ consists of a reddish-brown brittle resin, which, when distilled with zinc-dust, gives a-methylanthracene, and when treated with zinc-dust in alkaline solution behaves as a derivative of *methylanthraquinone*. Dilute alkalis dissolve it with a purple-violet coloration, and the corresponding salts are obtained as violet precipitates on adding sodium or potassium chlorides to these solutions. According to Perkin and Hummel, ventilagin is possibly allied to alkannin $C_{15}H_{14}O_4$, the colouring matter of alkanet, *Anchusa tinctoria* (Lam.), and may differ from this merely by the possession of two additional hydroxyl groups.

Emodin monomethyl ether $C_{16}H_{12}O_5$, m.p. 200°, consists of orange-red needles, and is identical with that subsequently isolated from the root of the *Polygonum cuspidatum* (Sieb. and Zucc.) (Perkin, Chem. Soc. Trans. 1895, 67, 1084). A similar, if not identical, substance was isolated by Schwabe (Arch. Pharm. 1888, 26, 569), and by Thorpe and Miller (Chem. Soc. Trans. 1892, 64, 6) from the bark of the *Rhamnus Frangula* (Linn.).

Trihydroxy-*a*-methylanthranole monomethyl ether (A) $C_{16}H_{14}O_4$, colourless needles, decomposes about 260° before melting, and is soluble in alkaline solutions with a yellowish-brown coloration. On gentle oxidation with chromic acid it is converted into emodin methyl ether, m.p. 200° (*l.c.*), and the same reaction takes place when its alkaline solution is oxidised with hydrogen peroxide.

Trihydroxy-*a*-methyl anthranole monomethyl ether (B) $C_{16}H_{14}O_4$, pale yellow needles, m.p. 173°, when oxidised with chromic acid is also converted into the emodin methyl ether, m.p. 200°. As two *a*-methylanthranols are capable of existence, the isomerism of these compounds may possibly be thus explained.



Substance $C_{16}H_8O_8$, orange-red crystalline powder, m.p. 275°–280°, is soluble in alkaline solutions with an orange-red coloration, and when heated with zinc-dust gives a hydrocarbon which resembles *a*-methylanthracene.

Substance $C_{17}H_{12}O_5$ (?) is a chocolate, crystalline powder, soluble in dilute alkalis with a yellow coloration, and these solutions, on exposure to air, deposit a blue amorphous precipitate.

Dyeing properties. On striped printed calico the root bark gives with alumina mordant a claret red, not unlike that of alizarin bordeaux; with iron mordant a greyish lilac, which in strong colours approaches a black; and with a mixture of the two a very purplish dark chocolate. The colours are moderately fast to soap, although considerably behind the alizarin colours in this respect. On oil prepared calico ventilago gives with alumina mordant a rich claret brown, with chromium mordant a very black purple, and with iron mordant a good purplish black shade. On wool chromium mordant gives a good purplish brown, alumina a bordeaux red, tin a brighter red similar to an alizarin red with alumina mordant, and iron mordant gives dark dull purple and black. On silk similar colours are produced. No difficulty is experienced in dyeing with ventilago, and no additions to the dye-bath are necessary, except in the case of wool, with which it is desirable to add calcium acetate in order to correct the strong acidity of the mordanted fibre. Owing to the slight solubility of the colouring matter in water, the dyeing does not commence until the temperature reaches 70°–80°. The root bark appears to contain from 8 to 10 p.c. of ventilagin. A. G. P.

VENETIAN CHALK *v.* STEATITE.

VENETIAN LAKE. *Crimson lake v.* PIGMENTS.

VENETIAN RED. Ferric oxide.

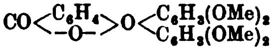
VENETIAN WHITE. A white lead pigment containing a large percentage of barium sulphate.

VERATRINE *v.* VEGETO-ALKALOIDS.

VERATROLE (o-*dimethoxybenzene*)

$$C_6H_4(OMe)_2$$

is best obtained by dissolving catechol (100 grms.) in methyl alcohol (200 grms.) mixed with 75 grms. of methyl sulphate. The mixture is cooled to −5°, and 150 grms. of potash dissolved in 350 grms. of water are then added all at once. In 3 mins. the methylation is complete. The product is diluted with water, extracted with ether, and the extract is dried and distilled (Perkin and Weizmann, Chem. Soc. Trans. 1906, 1656). Veratrole is also formed by the distillation of guaiacol with lead oxide (Pschorr and Silberbach, Ber. 1904, 37, 2149). Veratrole forms a crystalline mass, m.p. 15°, b.p. 205°. It yields a number of halogen derivatives (Cousin, Compt. rend. 1898, 127, 759; 1902, 135, 967; Ann. Chim. Phys. 1898, [vii.] 13, 483); also nitro derivatives (Cousin, Compt. rend. 1902, 134, 290; 135, 967; Salway, Chem. Soc. Trans. 1909, 1163), a *phthalide*



$$CO<\begin{matrix}C_6H_4\\-O-\end{matrix}>O<\begin{matrix}C_6H_3(OMe)_2\\C_6H_3(OMe)_2\end{matrix}$$

(Perkin and Weizmann, *l.c.*) and other compounds (Kropp and Decker, Ber. 1909, 42, 1184).

Veratrole reacts with hippuryl chloride in presence of aluminium chloride, forming a crystalline product, m.p. 155°

$$C_6H_3(OMe)_2CO{\cdot}CH_2{\cdot}NH{\cdot}COPh,$$

from which valuable therapeutic products are said to be obtained (D. R. P. 185596; Frdl. 1905–1907, 1184).

VERBENALIN. A crystalline glucoside found in *Verbena officinalis* (Linn.), m.p. 181·5°; $a_D = -180{\cdot}3°$. Hydrolysed by emulsin, yielding dextrose (Bourdier, J. Pharm. Chim. 1908, 27, 49, 101).

VERDIGRIS, VERT-DE-GRIS, VERT DE MONTPELIER. *Basic acetates of copper v.* ACETIC ACID.

VERDITER, GREEN AND BLUE, *v.* COPPER.

VERIDIAN. *Guignet's green v.* CHROMIUM.

VERJUICE. A kind of vinegar containing malic acid made from the juice of the crab-apple.

VERMILION *v.* MERCURY.

VERMILIONETTE. A red pigment made by adding eosin to white lead, barium sulphate or zinc white.

VERONAL. Trade name for diethylmalonylurea $(C_2H_5)_2C[CO{\cdot}NH]_2CO$, prepared by the condensation of urea and diethyl malonyl chloride. A white crystalline powder of bitter taste, m.p. 191°. Soluble in water, ether, acetone, acetic ester. Used as a soporific (*v.* SYNTHETIC DRUGS and PYRIMIDINES).

VERT DE GUIGNET *v.* CHROMIUM.

VESIPIRIN. Trade name for phenyl acetosalicylate, *v.* SALICYLIC ACID and SYNTHETIC DRUGS.

VESTORIEN *v.* EGYPTIAN BLUE; also ENAMELS.

VESUVIANITE or **IDOCRASE.** A mineral consisting of a complex silicate of calcium and aluminium, together with iron, magnesium, water, fluorine, boron, &c. F. W. Clarke's formula is $R'_4Al_2Ca_7Si_6O_{24}$, where $R'_4 = Ca_2, (AlOH)_2, H_4$, &c. Crystals are tetragonal and usually green or brown in colour, sp.gr. 3·35–3·45; H. 6½.

The mineral is of common occurrence in contact-metamorphic rocks, particularly crystalline limestones. Lustrous, brown crystals are common at Monte Somma, Vesuvius (hence the name vesuvianite). Green crystals from Ala in Piedmont are cut as gems at Turin. A compact, massive variety has been found abundantly as blocks and boulders, measuring up to 6 by 3 ft., at several places in California (Siskiyou, Butte, Fresco, and Tulare counties). This has been called *californite* (G. F. Kunz, 1903), and is much used as a gem-stone and for larger ornamental objects. It is somewhat translucent, takes a high polish, and ranges from bright green to yellowish-green and white in colour, thus closely resembling jade in appearance (D. B. Sterrett, Min. Res. U.S., annual reports for 1909 and 1910). L. J. S.

VICIANIN *v.* GLUCOSIDES.

VICIANOSE *v.* CARBOHYDRATES.

VICTORIA YELLOW. *Gold yellow, Aniline orange, Saffron surrogate.* This colouring matter, introduced by Mettenzwei, under the name of *Victoria yellow* or *aniline orange* (Wag. Jour. 1869, 593), consists of the potassium or ammonium salt of a dinitrocresol (Martius and Wichelhaus, Ber. 2, 206; v. Sommaruga, *ibid.* 2, 579). It is prepared by heating cresol, boiling at about 795°, with three times its weight of sulphuric acid at 100°, until the product is soluble in water. After removing the excess of sulphuric acid by means of barium carbonate, the cresolsulphonic acid is converted into potassium salt, which in the dry state is nitrated by introducing it rapidly into about three times its weight of dilute nitric acid (sp.gr.=1·2), and is then poured into water, neutralised with potassium carbonate, and the resulting potassium dinitrocresol crystallised out. Obtained in this way, the colouring matter is a mixture of the potassium salts of dinitro-*o*- and dinitro-*p*-cresol, and varies in colour according to the proportions of these. Thus Victoria yellow is yellowish in colour, and consists chiefly of the potassium salt of dinitro-*o*-cresol (m.p.=86°), which crystallises in yellow needles (Wichelhaus, *ibid.* 7, 176; Piccard, *ibid.* 8, 685), whereas saffron surrogate is distinctly reddish in colour, and consists chiefly (80 p.c. according to Piccard) of the potassium salt of dinitro-*p*-cresol (m.p.=84°), which crystallises in red needles (Armstrong and Field, Chem. News, 27, 318; Hofmann and v. Miller, Ber. 14, 567; Staedel, *ibid.* 14, 900, 906; Nölting and Salis, *ibid.* 14, 986).

Victoria yellow is soluble in water and dyes wool and silk orange, but owing to the fugitive nature of the colour is no longer employed for this purpose. Saffron surrogate is still used to some extent as a colouring matter for butter, margarine, vermicelli, cheese, &c. (Piccard), but this is to be deprecated, since Weyl's experiments show that the compound is poisonous (Ber. 20, 2835; 21, 512). *Cf.* NITITROPHENOLS AND THEIR HOMOLOGUES.

VIENNA BLUE. *Cobalt blue v.* PIGMENTS.

VIENNA GREEN. *Emerald green v.* PIGMENTS.

VIENNA PASTE. A mixture of lime and potash used as a caustic to extirpate malignant growths.

VINASSE *v.* SUGAR.

VINE BLACK. *Blue black v.* PIGMENTS.

VINEGAR, AROMATIC, *v.* ACETIC ACID.

VINEGAR PLANT *v.* ACETIC ACID; FERMENTATION.

VINOLINE. A mixture of coal-tar reds, mostly rosaniline salts, used for colouring wines.

VINOPYRIN *v.* SYNTHETIC DRUGS.

VIOFORM. Trade name for iodochlorohydroxyquinoline. A greyish-green powder used as a bactericide and antiseptic, and as a substitute for iodoform (*v.* SYNTHETIC DRUGS).

VIOLANTHRENE *v.* INDANTHRENE.

VIOLET DE PARIS or **VIOLET DIRECT.** *Methyl violet v.* TRIPHENYLMETHANE COLOURING MATTERS.

VIOLET 5 B, 6 B, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

VIOLET R and **R R** and **5 R.** *Hofmann's violet v.* TRIPHENYLMETHANE COLOURING MATTERS.

VIOLIN. An emetic substance contained in the common violet, supposed to be identical with emetine from ipecacuanha root.

VIOLINE or **VIOLEÏN.** A synonym for mauve or aniline purple.

VIOLURIC ACID *v.* PYRIMIDINES.

VIRIDIAN. Hydrated chromium sesquioxide, *v.* CHROMIUM.

VIRIDINIC ACID *v.* TANNINS.

VISCOSE *v.* SILK, ARTIFICIAL.

VITELLIN *v.* PROTEÏNS.

VITEXIN. The *Vitex littoralis* (A. Cunn.) or 'Puriri' is a large tree, 40–60 ft. high, and 3–5 ft. in diameter, which grows only in the northern portion of the North Island of New Zealand. The wood affords a very durable timber, and is chiefly used for house blocks, fencing posts, piles for bridges, railway sleepers, &c.

Vitexin, the main colouring matter, is present in the wood in the form of a glucoside which has not yet been isolated. It is prepared by digesting a purified extract of the dyestuff with boiling dilute hydrochloric acid, and by this means separates in the form of a yellow viscous mass. By extracting this crude product with boiling alcohol a pale yellow crystalline powder remains undissolved, and this, owing to its sparing solubility, is most readily purified by acetylation, and the subsequent hydrolysis of the pure acetyl derivative (Perkin, Chem. Soc. Trans. 1898, 74, 1020).

Vitexin consists of minute canary-yellow prismatic or fine hair-like needles, soluble in alkaline solutions with a pale yellow coloration, and from these solutions when boiled it is deposited by acidification in a crystalline condition.

On fusion with alkali vitexin yields *phloroglucinol* and p-*hydroxybenzoic acid*, and when digested with boiling 50 p.c. potassium hydroxide solution p-*hydroxyacetophenone* is also produced. Boiling 15 p.c. nitric acid gives *dinitro*-p-*hydroxybenzoic acid*, together with a small quantity of *tetranitroapigenin*, m.p. 239°–241°. The formula first assigned to vitexin by Perkin was $C_{15}H_{14}O_7$, and the *acetyl* derivative, colourless prismatic needles, m.p. 251°–256°, was consequently represented as $C_{15}H_9O_7(C_2H_3O)_5$. In a later communication in view of its relationship to apigenin, and the difficulty of accounting for the large number of hydroxyl groups which are present, it is suggested by this author (Chem. Soc. Trans. 1899, 77, 422) that vitexin is probably a very stable glucoside of apigenin represented by the formula $C_{21}H_{20}O_{10}$. Vitexin is a somewhat feeble colouring matter, and dyes shades similar to those given by apigenin; these employing woollen cloth mordanted with chromium, aluminium, and tin, are respectively greenish yellow, pale bright yellow, and pale brown.

In addition to vitexin the wood of *Vitex littoralis* contains (as glucoside) a small quantity of a second colouring matter *homovitexin*. It was obtained as a pale yellow powder, m.p. 245°–246°, and is distinguished from vitexin by its ready solubility in alcohol. Fused with alkali it gives *phloroglucinol* and p-*hydroxybenzoic acid*, and is possessed of feeble dyeing property. The analytical figures approximate to $C_{16}H_{16}O_7$ or $C_{18}H_{18}O_8$.

According to Barger (Chem. Soc. Trans. 1906, 89, 1120) the glucoside saponarin, which is present in the *Saponaria officinalis* (Linn.) yields on hydrolysis glucose, saponaretin, and a small quantity of vitexin. It is possible that saponaretin and homovitexin are identical.

A. G. P.

VITRIFIABLE PIGMENTS *v.* POTTERY; also PORCELAIN.

VITRIOL (*vitrum*, 'glass'). An old name for a sulphate, and still frequently applied to the sulphates of certain common metals on account of their vitreous lustre, *e.g.* white or zinc vitriol $ZnSO_4,7H_2O$; blue or copper vitriol $CuSO_4,5H_2O$; green or iron vitriol $FeSO_4,7H_2O$; red or cobalt vitriol $CoSO_4,7H_2O$. Basic ferric or ferroso-cupric sulphates obtained in the extraction of copper sulphate from ferruginous minerals are known as Admont, Bayreuth, Salzburg vitriols, &c.

VITRIOL, OIL OF. *Vitriolic acid.* Sulphuric acid (*q.v.*).

VITRIOL STONE and **COLCOTHAR.** Vitriol is the material from which the so-called fuming or Bohemian sulphuric acid was formerly manufactured, and it is obtained from the rock known as vitriol slate ('vitriolschiefer') in the following manner. Large masses of pyritous slate (which belongs to the Silurian formation, and consists of a quartzose matrix containing pyrites, carbon, and clay) are exposed to the weathering action of the atmosphere for three years. The products of oxidation so formed are ferrous sulphate and sulphuric acid, which latter acts upon the clay, yielding aluminium sulphate and other sulphates. The ferrous sulphate at first formed becomes by oxidation ferric sulphate, which, together with the aluminium sulphate, is the principal product of the weathering of the vitriol slate. Ferrous sulphate remains only in small quantities. The next operation is lixiviation of the mass with water, after which the liquor obtained is concentrated to a density of 40°B., and finally evaporated in pans until, on cooling, a crystalline cake of vitriol stone is obtained. The vitriol stone is now calcined, in order to remove the greater part of its water. The resulting product, when heated to a high temperature in clay retorts, yields sulphur trioxide; and a residue, termed *colcothar*, remains in the retorts. The composition of vitriol stone and colcothar may be seen from the following analyses:—

Vitriol stone. Fe_2O_3 20·07, Al_2O_3 4·76 FeO 0·64, MnO traces, CaO 0·14, MgO 0·39, K_2O 0·07, Na_2O 0·05, CuO 0·10, SiO_2 0·10, P_2O_5 traces, SO_3 40·51, As traces, H_2O 32·58. Total 99·32; or combining acid oxides and bases: $Fe_2(SO_4)_3$ 50·17, $Al_2(SO_4)_3$ 11·94, $FeSO_4$ 1·35, $MgSO_4$ 1·17, $CaSO_4$ 0·33, $CuSO_4$ 0·20, K_2SO_4 0·13, Na_2SO_4 0·11, H_2SO_4 1·49, MnO, As, and P_2O_5 traces, SiO_2 9·10, H_2O 3·31–99·29.

Colcothar. Fe_2O_3 7·62, Al_2O_3 12·53, MgO 3·23, CaO 0·82, SO_3 5·17, SiO_2 1·17, CuO 0·20, H_2O 1·30–99·04 (F. Stolba, B. Königl. Böhm. Gesells. 1885; J. Soc. Chem. Ind. 6, 30).

VIVIANITE *v.* BLUE IRON-EARTH.

VOLBORTHITE *v.* VANADIUM.

VOLEMITOL *v.* CARBOHYDRATES.

VOLUMENOMETER *v.* SPECIFIC GRAVITY.

VOROBYEVITE *v.* BERYL.

VRAIC. *Varech.* The French name for kelp, *v.* IODINE.

VULCANISED OILS *v.* OILS, FIXED, and FATS.

VULCANITE *v.* RUBBER. Also applied to a nitroglycerin explosive.

VULCAN POWDER *v.* EXPLOSIVES.

VULPIC or **VULPULIC ACID** *v.* LICHENS.

VULPINITE. A variety of anhydrite mixed with silica. That from Vulpino near Bergamo, known as the *Marmo Bardiglio di Bergamo*, takes a fine polish and is used for ornamental purposes.

W

WAD or **BOG-MANGANESE.** A black, earthy mineral consisting mainly of hydrated manganese dioxide, but of variable composition, barium and various other constituents being often present. Many varieties have consequently been distinguished by special names. *Asbolite* or 'earthy cobalt' is a cobaltiferous variety, and *lampadite* contains copper. The mineral may be regarded as an earthy form of psilomelane (*q.v.*); it is so soft and sooty that it soils the fingers, and is sometimes so porous that it floats on water. It has resulted by the weathering and decomposition of other manganese minerals, and is sometimes deposited from solution by springs and in swamps. It is of wide distribution and is mined at many places together with other oxides of manganese. Asbolite is of importance as an ore of cobalt (up to 35 p.c. CoO), as much as 5000 tons per annum having been exported from New Caledonia.

L. J. S.

WALNUT HUSKS (*Brous des noix*, Fr.) are employed by the French dyers to give dun colours. The green shells contain *juglone* or *hydroxy*-[*a*]-*naphthaquinone*; *v.* NAPHTHALENE.

WALNUT OIL *v.* OILS, FIXED, AND FATS.

WALSRODE POWDER *v.* EXPLOSIVES.

WARAS, also called 'wars' and 'wurrus,' consists of a purplish, resinous powder which covers the seed pods of *Flemingia congesta* (Roxb.), an erect woody shrub growing in the thickets and forests of the warmer part of India. According to Watt (Dictionary of Economic Products of India, iii. 482), it is collected also in Africa in the neighbourhood of Harrar, and is sent to Arabia, chiefly to Yemen and Hadbramant, where it is used as a dye, as a cosmetic, and as a specific against colds. According to Wardle, waras is distinctly inferior as a dye to kamala, which it closely resembles, and contains only a small amount of colouring matter compared with the yellow vegetable dyes of commerce. It is suitable as a dye for silk rather than for wool, but is quite useless with cotton. It has been introduced into England from Aden as an adulterant or substitute for kamala (Flückiger and Hanbury's Pharmacographica, 1879, 576). Under the microscope waras appears as orange-brown lumps, frequently circular and closely resembling kamala.

Flemingin $C_{12}H_{12}O_3$ (provisional) is a dull orange-red crystalline powder consisting of star-shaped groups of minute prismatic needles, which melt at 171°–172°, and closely resembles the rottlerin of kamala. Solutions of the alkali hydroxides dissolve it with an orange-brown tint, but these solutions when boiled do not deposit resinous matter, as is the case with rottlerin. On fusion with alkali salicylic acid and acetic acid are produced.

Silk suspended in a solution of flemingin in dilute sodium carbonate, and the whole gradually raised to the boiling temperature, is dyed golden yellow slightly duller than the shade given by rottlerin; but, on the other hand, flemingin possesses much the stronger dyeing power of the two.

In addition to flemingin waras contains a trace of a yellow crystalline colouring matter, *homoflemingin*, m.p. 165°–166° (C=69·97; H=5·75), together with some quantity of two resinous substances: (*a*) $C_{12}H_{12}O_3$, m.p. 162°–167°, and (*b*) $C_{13}H_{14}O_3$, melting below 100°. Fused with alkali these latter gave salicylic and acetic acids, and appear to be allied to flemingin.

Added to a boiling solution of its own weight of sodium carbonate, waras dyes silk golden yellow shades, which are brightened by rinsing in very dilute acetic acid. Contrary to the statement of Wardle, it is to be regarded as a decidedly superior dyestuff to kamala (Perkin, Chem. Soc. Trans. 1898, 73, 659). A. G. P.

WASH. The name given to the fermented wort of the distiller.

WATER. Water is absolutely indispensable to both animal and vegetable life; it is the cause of many of the most striking phenomena in nature, and is employed for countless purposes by man. Its distribution is as wide as that of the air itself, whilst its amount on the earth is enormously greater. In an absolutely pure state it is never met with in nature. The impurities in natural water are derived from the materials—solid, liquid, or gaseous—with which it comes in contact, and they may be present either in suspension or in solution or in both. Inasmuch, therefore, as the interest attaching to different waters depends upon the impurities they contain, and these are dependent upon the matters with which they have been in contact, it is most convenient to classify waters according to their origin.

1. *Rain-water, snow, hail, dew, and hoar-frost.* All these forms of water are obtained by the condensation of the aqueous vapour which is invariably present in the air. The amount of aqueous vapour which can be contained in a given volume of air is solely dependent upon the temperature. If the atmosphere has become saturated with aqueous vapour at any given temperature and is cooled below that temperature, the excess of aqueous vapour will condense, according to circumstances, as rain, hail, snow, mist, dew, or hoar-frost. This condensation is promoted by the presence of dust and electrically charged particles. All these forms of water having been only in contact with the air and not with the earth are characterised by the small proportion of solid matter which they contain, although the amount found, especially in the vicinity of towns, is often considerably greater than would be anticipated, and the rain-water falling in the neighbourhood of the sea is often mixed to a considerable extent with sea-spray, which with favourable winds is carried many miles inland. In the following table are recorded the maximum, minimum, and average proportions of the several ingredients in samples of rain-water collected at Rothamsted and elsewhere, expressed in parts per 100,000—

—	Total solid impurity	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Chlorine	Hardness
Minimum . . .	0·62	0·021	0·003	0·005	0	0	0
Maximum . . .	8·58	0·372	0·121	0·155	0·044	1·65	1·7
Average . . .	3·42	0·095	0·021	0·049	0·007	0·33	0·5
Rain-water collected at Land's End, Cornwall, Jan. 2, 1873 . .	42·80	0·131	0·034	0	0·020	21·8	10·0
Rain-water collected near Hyde Park, London, Nov. 8, 1873 . .	2·76	0·383	0·040	0·210	0·008	0·5	1·1

It is thus seen that the composition of rain-water, even in the open country, is liable to great fluctuations, and that the amount of impurity, both mineral and organic, is occasionally surprisingly large. The amount of organic impurity in dew and hoar-frost is even still greater owing to these forms of water being condensed out of the lowest and most-contaminated couches of the atmosphere. Thus—

SEVEN SAMPLES OF DEW AND HOAR-FROST, ROTHAMSTED, 1869 AND 1870.

(Results of Analysis expressed in parts per 100,000.)

——	Total solids	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Chlorine	Hardness
Minimum	2·64	0·195	0·026	0·130	0	0·35	1·3
Maximum	8·00	0·450	0·196	0·280	0·050	0·80	2·5
Average	4·87	0·264	0·076	0·198	0·023	0·53	1·9

Two other impurities, not referred to above, which are generally present in the rain-water and snow of towns are sulphurous and sulphuric acids derived from the combustion of coal. Angus Smith found in the rain-water of London 2·05, of Liverpool 3·06, in that of Manchester 4·48, and in that of Glasgow 7·02 parts of sulphuric acid per 100,000, to a considerable extent in the free state. Sendtner found freshly-fallen snow in Munich to contain 0·7 part sulphuric acid (SO_3) per 100,000, on the following day 1·76 parts, after 10 days 6·22 parts, and after 16 days 9·18 parts. The presence of this free acid in the rain-water of towns is, of course, not only detrimental to vegetation, but also to sculptures and buildings in which marble or limestone are employed. The proportion of ammonia increases in the snow after lying on the ground (Wagner, Technologie, 305).

2. *Upland surface water* most nearly approaches in composition to that of the atmospheric waters dealt with in the last section. It is, in fact, rain-water which has undergone minimum contact with the earth, although in consequence of its solvent action even this contact is sufficient to impart to the water in many cases such proportions of dissolved matter as are never found in rain-water. The amount and nature of these ingredients depend, of course, mainly upon the kind of soil over which the water has travelled, and consequently it becomes convenient to sub-divide this class according to the geological character of the ground from which the upland surface water has been obtained.

In the following tables are recorded the maximum, minimum, and average amounts of impurity found in the examination of a large series of samples of waters principally derived from land not under cultivation, so as to represent the characters naturally acquired by water passing over the various geological formations.

I.—WATERS FROM NON-CALCAREOUS STRATA.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
(*a*) *Upland surface water from Igneous rocks.*[1]										
Maximum . .	12·70	0·582	0·071	0·004	0·029	0·073	2·10	0·4	5·7	5·9
Minimum . .	1·52	0·074	0·013	0	0	0·014	0·35	0	0·8	0·8
Average (18 samples)	5·15	0·278	0·033	0·001	0·002	0·035	1·13	0·1	2·0	2·1
(*b*) *Upland surface water from Metamorphic, Cambrian, Silurian, and Devonian rocks.*[2]										
Maximum . .	12·48	1·059	0·076	0·008	0·043	0·110	3·35	1·8	6·9	6·9
Minimum . .	2·14	0·042	0·001	0	0	0·002	0·52	0	0·3	0·4
Average (81 samples)	5·12	0·293	0·024	0·002	0·006	0·031	0·92	0·3	2·5	2·5
(*c*) *Upland surface water from Yoredale and millstone grits and non-calcareous portion of the coal measures.*[3]										
Maximum . .	15·00	1·457	0·103	0·024	0·042	0·116	1·59	3·7	8·1	8·7
Minimum . .	4·58	0·033	0	0	0	0·012	0·65	0	0·9	0·9
Average (47 samples)	8·75	0·377	0·033	0·003	0·010	0·050	1·05	0·4	4·3	4·7
(*d*) *Upland surface water from Lower London Tertiaries and Bagshot beds.*										
Maximum . .	13·14	0·439	0·056	0·012	0·020	0·086	2·60	0·9	5·6	5·6
Minimum . .	5·92	0·282	0·039	0	0	0·039	1·24	0	1·8	1·8
Average (3 samples)	8·40	0·379	0·048	0·004	0·007	0·058	2·06	0·3	3·5	3·8

---

[1] All soft and peaty. Generally turbid, and of a yellowish or even brownish colour.

[2] This water is also generally peaty, and often turbid and coloured. Owing to the large area of these rocks exposed they form some of the most important gathering grounds, especially in Scotland.

[3] Soft, but generally turbid, peaty, and of a yellow or brownish colour.

II.—Waters from Calcareous Strata.

(Results of Analysis expressed in parts per 100,000.

Description	Total solid matter	Organic carbon	Organic Nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
(a) Upland surface water from Silurian and Devonian rocks.[1]										
Maximum . .	14·46	0·475	0·046	0	0·055	0·080	1·62	3·5	9·6	9·6
Minimum . . .	12·26	0·103	0·008	0	0	0·016	0·83	0	5·2	7·5
Average (3 samples, all from Scotland) .	13·71	0·301	0·026	0	0·021	0·047	1·20	1·2	7·4	8·6
(b) Upland surface water from Mountain Limestone.[2]										
Maximum . .	23·40	0·812	0·097	0·002	0·042	0·097	1·59	9·3	10·6	14·6
Minimum . . .	12·45	0·218	0·023	0	0	0·024	0·92	1·7	4·3	9·8
Average (7 samples) .	17·07	0·370	0·047	0·001	0·011	0·059	1·24	5·7	7·0	12·7
(c) Upland surface water from calcareous portion of Coal Measures.[3]										
Maximum . .	77·36	0·856	0·089	0·010	0·061	0·122	4·85	11·6	13·6	25·0
Minimum . . .	10·20	0·082	0·001	0	0	0·014	0·84	0	3·0	6·2
Average (26 samples) .	22·79	0·346	0·037	0·003	0·016	0·056	1·52	4·0	8·3	12·3
(d) Upland surface water from Lias, New Red, and Conglomerate Sandstone.										
Maximum . .	26·32	0·506	0·075	0·008	0·034	0·100	2·00	16·0	12·9	24·8
Minimum . . .	11·08	0·186	0·020	0	0	0·022	0·99	2·9	3·1	6·0
Average (8 samples) .	18·92	0·300	0·042	0·002	0·012	0·056	1·50	7·8	6·3	14·0
(e) Upland surface water from Magnesian Limestone.[4]										
Ripon, the Kex Beck, 8 miles from source, Jan. 27, 1874 .	17·84	0·172	0·036	0·001	0	0·037	1·40	6·4	8·3	14·7
(f) Upland surface water from Oolites.[5]										
The Frome, above Woodlands Mill, Somersetshire, March 10, 1870 .	17·46	0·326	0·025	0·004	0·042	0·070	1·55	6·6	5·8	12·4

[1] Owing to the compact nature of the limestone in these old formations, the hardness is very moderate.

[2] Hardness not excessive, but large amount of organic matter (peaty), rendering the waters coloured and unpalatable.

[3] Of very variable character; generally of only moderate hardness, but containing much peaty matter, and hence coloured and unpalatable.

[4] Slightly turbid.

[5] Slightly turbid. Owing to the porous nature of Oolite formation, surface water is very rare.

The above analyses show that upland surface waters generally contain a considerable amount of dissolved matters only when they are derived from calcareous strata. The organic matter is subject to great variation, but in every case contains only a very small proportion of nitrogen in comparison with the carbon, indicating that the organic substances present are of vegetable origin, which is further attested by the almost entire absence of ammonia, nitrates, and nitrites, all of which, when present in amount beyond that in which they occur in rain-water, are nearly exclusively derived from the decomposition of animal matters. The chlorine is also low, the upland gathering grounds being generally beyond the reach of sea-spray and not receiving the liquid excrements of animals, which are particularly rich in chlorides, whilst from their mere surface contact with the soil they have not extracted any considerable quantities of the salts present in the latter, as is the case with spring- and well-water.

3. *Surface water derived from cultivated land.* This includes the great body of river-waters, inasmuch as practically all streams flow through and receive accessions from land under cultivation before reaching the sea. The composition of such waters is very varied, depending upon local circumstances, and being liable to great fluctuations at different seasons of the year. This group may be conveniently divided into two sub-groups, according as the water is derived from calcareous or non-calcareous districts. The following results of analyses of British waters of this description are compiled from the Sixth Report of the Rivers Commission, 1874:—

SURFACE WATERS FROM CULTIVATED LAND.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
			(*a*) *Water from non-calcareous districts.*[1]							
Maximum . .	18·10	1·124	0·112	0·056	0·258	0·393	2·80	4·6	8·0	10·1
Minimum . . .	5·26	0·125	0[2]	0	0	0·017	0·70	0	1·8	2·1
Average (31 samples) .	9·52	0·276	0·034	0·007	0·089	0·128	1·49	0·6	4·3	4·9
			(*b*) *Water from calcareous districts.*[3]							
Maximum . .	110·40	1·338	0·307	0·030	1·005	1·096	12·75	26·3	42·1	67·3
Minimum . . .	13·22	0·069	0·009	0	0	0·033	0·54	0	2·1	7·8
Average (144 samples)	30·08	0·268	0·053	0·005	0·257	0·314	2·24	12·4	8·2	20·6

[1] Usually turbid, organic matter generally moderate in amount, but partially of animal origin.

[2] This result is extremely improbable, more especially as the particular water in question (a sample of the water supplied to Bury and Radcliffe, Lancashire) contained 0·229 organic carbon, 0·032 ammonia, and 0·066 nitrogen as nitrates and nitrites.

[3] Generally turbid, the organic matter is much the same in amount as in the water from non-calcareous districts, but generally more nitrogenous, in consequence of calcareous soils being usually under higher cultivation than non-calcareous ones. The total combined nitrogen is also for the same reason considerably greater, and the hardness is, of course, very much higher.

In connection with the effect of cultivated and upon the water which comes in contact with it, it is instructive to note the nature of the water which drains from such land, as this throws light upon the composition of subterranean waters (from springs and wells), which will be considered below.

In the following table is recorded the composition of the water obtained from drain-pipes placed from 18 ins. to 5 ft. below a plot of land at Rothamsted which had remained both unmanured and uncropped for a period of 11–15 years :—

COMPOSITION OF WATER FROM LAND UNMANURED AND UNCROPPED FOR ELEVEN TO FIFTEEN YEARS.[1] (6th Rep. Riv. Com. p. 62.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . .	63·28	0·235	0·116	0·026	4·936	4·981	3·80	7·2	11·9	16·6
Minimum . .	18·00	0·096	0·026	0	0·607	0·654	0·60	0·3	3·2	3·5
Average (15 samples distributed over four years) . .	32·06	0·154	0·053	0·006	2·195	2·253	1·65	4·1	8·5	12·6

[1] The samples varied from clear to turbid.

It will be seen that the conversion of the original nitrogenous organic matter in the soil nto mineral products is a very slow process, large quantities of nitrates being still present in the drainage waters after the lapse of so many years.

It is interesting to compare with the above the composition of the water draining from a plot of land unmanured for 16–21 years, but continuously bearing an annual wheat crop during that time :—

COMPOSITION OF WATER FROM LAND UNMANURED FOR SIXTEEN TO TWENTY-ONE YEARS, BUT CONTINUOUSLY BEARING WHEAT CROPS. (6th Rep. Riv. Com. p. 60.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . .	48·40	0·242	0·058	0·006	2·268	—	3·80	14·1	22·4	32·7
Minimum . .	13·80	0·099	0·010	0	0	—	0·80	8·9	3·9	13·5
Average (11 samples distributed over five years) . .	24·96	0·170	0·034	0·002	0·645	—	1·37	10·8	8·4	19·2

As might have been anticipated, the proportions of ammonia and nitrates finding their way into the drainage water in this case were much less, and in the summer months during the growth of the crop the amount of this mineral nitrogen found in the drainage water was practically *nil.*

We will, in the next place, compare with the above the composition of the drainage water from land which had been manured annually with 14 tons of farmyard manure per acre over a period of 24–29 years, and bearing wheat continuously during that time :—

Composition of Drainage Water from Land manured with 14 Tons Farmyard Manure per Acre for Twenty-four to Twenty-nine Years. (6th Rep. Riv. Com. p. 58).

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . .	51·20	1·243	0·335	0·052	2·592	2·754	3·35	12·1	20·6	32·1
Minimum . .	14·00	0·181	0·036	0	0·082	0·130	0·60	1·4	5·4	8·7
Average (13 samples over five years) .	25·90	0·519	0·115	0·009	0·528	0·665	1·30	6·8	8·6	15·4

Thus the difference between the drainage waters from the unmanured and manured land is not nearly so great as might have been expected, being principally confined to the larger proportion of organic matter found in the latter.

The above results may be compared with those obtained in the analysis of a number of samples of the drainage water from sewage farms, in all of which the town sewage is, or was, applied to land, with the double object of purifying the sewage and deriving a profit out of the crops raised. Thus :—

Composition of Drainage Water from Sewage Farms. (6th Rep. Riv. Com. pp. 55–57.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . .	103·00	2·160	0·517	1·366	6·499	6·833	13·40	36·9	39·3	56·6
Minimum . . .	18·60	0·108	0·034	0·005	0	0·069	2·15	0	3·9	3·9
Average (72 samples)	64·02	0·982	0·191	0·388	0·756	1·266	6·36	17·6	15·4	33·0

It will be seen that the drainage water from sewage farms is generally richer in organic and inorganic impurities than the water draining from manured or unmanured land, the passage of the water through the ground being in the latter case a much slower one, and thus allowing time for more perfect purification by soil and plants. Occasionally, as indicated by the above minimum results, the drainage water from sewage farms is remarkably free from impurities. A much purer drainage water is often yielded in the intermittent downward filtration of sewage through suitable land.

The knowledge thus gained of the composition of waters draining from cultivated land becomes of special value in studying the nature of the next group of waters (shallow well water).

4. *Shallow well water.* It has been estimated that about twelve millions of the inhabitants of Great Britain are supplied with water for domestic purposes from shallow wells. This class of water is very liable to serious contamination with sewage and refuse animal matters, inasmuch as such wells are almost invariably sunk in the vicinity of human dwellings, and frequently within a few feet of the cesspool receiving their drainage. It is these waters which have most frequently caused serious outbreaks of typhoid fever. In consequence of the great practical interest attaching to these waters, their composition will be considered in connection with the principal geological formations upon which such shallow wells may be sunk.

The results recorded on the next page serve to show the general composition of shallow well waters as met with in Great Britain. The composition of these waters varies within very wide limits, even when derived from one and the same geological formation, which is due to their being not generally an aqueous extract of a soil in its natural condition, but of ground which is often saturated with sewage and other animal refuse. In consequence of the oxidising power of soil, the organic matter of this refuse is not unfrequently almost entirely destroyed before reaching the wells, and even the ammonia which is one of the first products of its decomposition, has often disappeared, having generally become converted into nitrates and nitrites. Of nitrates and nitrites these shallow well waters generally contain some, and often a large amount, which thus, together with the ammonia

Shallow Well Waters.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Gneiss and Silurian rocks [1] (6th Rep. Riv. Com. p. 69).										
Maximum	100·20	0·362	0·110	0·625	2·465	3·090	17·00	22·3	19·2	41·5
Minimum	6·32	0·027	0·003	0	0·033	0·040	0·90	0	3·3	3·4
From Devonian rocks [2] (29 samples analysed).										
Maximum	105·20	0·794	0·172	0·630	4·197	4·261	17·00	18·3	47·8	55·7
Minimum	12·16	0·004	0·003	0	0·033	0·039	1·60	0	3·2	5·0
From Yoredale and Millstone grits [3] (20 samples analysed).										
Maximum	133·60	0·859	0·216	0·010	5·100	5·200	13·90	37·2	65·1	90·0
Minimum	5·92	0·039	0·007	0	0·006	0·013	0·65	0	2·9	2·9
From Coal measures [4] (44 samples analysed).										
Maximum	220·92	1·200	0·169	0·170	10·102	10·262	29·00	28·2	112·6	140·8
Minimum	9·40	0·024	0·007	0	0	0·015	0·99	0	1·4	3·4
From Mountain Limestone and Magnesian Limestone [5] (9 samples analysed).										
Maximum	108·88	0·190	0·070	0·002	4·812	4·884	13·35	40·1	48·5	88·6
Minimum	45·84	0·037	0·010	0	0·527	0·549	2·40	18·3	21·8	40·7
From New Red Sandstone [6] (87 samples analysed).										
Maximum	240·20	2·349[7]	0·346[7]	0·620	14·717	15·333	39·00	52·0	99·6	127·1
Minimum	20·64	0·029	0·009	0	0	0·027	1·40	0	3·8	17·1
From Lias [8] (38 samples analysed).										
Maximum	306·85	1·792	0·298	0·152	19·858	20·123	40·50	40·1	111·0	116·9
Minimum	49·48	0·052	0·023	0	0	0·033	1·75	0	1·2	2·7
From Oolites [9] (25 samples analysed).										
Maximum	269·60	2·662	0·531	0·240	12·220	12·508	44·50	42·6	55·9	78·9
Minimum	31·00	0·041	0·008	0	0	0·178	1·23	10·8	3·1	23·0
From Upper and Lower Greensand and Wealden [10] (21 samples analysed).										
Maximum	381·10	0·485	0·196	0·160	6·722	6·735	82·50	35·8	44·7	80·5
Minimum	10·52	0·014	0·006	0	0	0·012	2·10	0	3·8	3·8
From Chalk [11] (33 samples analysed).										
Maximum	159·16	0·772	0·340	1·700	6·345	7·779	28·50	39·7	47·1	71·5
Minimum	32·48	0·014	0·007	0	0·613	0·628	1·79	12·0	5·6	23·6
From gravel on the London Clay [12] (49 samples analysed, 37 from London itself).										
Maximum	396·50	1·006	0·604	2·750	25·840	25·927	34·60	49·2	164·3	191·0
Minimum	31·80	0·040	0·012	0	0	0·013	1·90	0	5·7	14·3
From Bagshot beds [13] (8 samples analysed).										
Maximum	286·80	1·295	0·154	0·630	17·940	—	31·15	21·5	111·9	131·7
Minimum	23·18	0·078	0·027	0·001	0	0·087	2·48	5·4	5·6	13·1
From Fluvio-marine series [14] (13 samples analysed).										
Maximum	66·12	0·429	0·093	0·016	3·640	3·734	7·20	12·1	29·3	36·4
Minimum	8·16	0·063	0·010	0	0	0·010	2·40	0	4·6	4·6
From Alluvium and gravel [15] (29 samples analysed).										
Maximum	320·72	0·931	0·940	3·050	11·265	14·300	36·25	36·4	118·6	152·4
Minimum	28·58	0·015	0·010	0	0	0·074	1·70	2·7	1·9	4·6

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[1] In almost all cases clear and palatable. [2] Generally clear and palatable. [3] Almost all clear and palatable.

[4] In many cases clear and palatable; but in others turbid, and even very turbid.

[5] All clear or slightly turbid and palatable.

[6] Generally clear, or only slightly turbid and palatable. In a few cases saline taste.

[7] Even this water clear and palatable. [8] In nearly all cases clear, or slightly turbid and palatable.

[9] Varying from clear and palatable to very turbid. In some cases saline taste.

[10] Mostly more or less turbid. Palatable.

[11] Clear to very turbid. Palatable, or occasionally slight saline taste.

[12] Generally more or less turbid and palatable. Occasionally slight saline taste.

[13] Generally more or less turbid and palatable. [14] More or less turbid and palatable.

[15] Generally clear or only slightly turbid and palatable. Occasionally slight saline taste.

testify to the water having previously been in contact with nitrogenous organic matter which has subsequently undergone destruction. In shallow well waters, even when the organic matter is only small in amount, it is generally highly nitrogenous, pointing to its probable animal origin, and in some exceptional cases the organic nitrogen found is actually in excess of the carbon. These waters, which are generally suspicious from the presence of mineral nitrogen, become in the highest degree dangerous when the proportion of organic matter is large.

5. *Deep well waters.* It is convenient to distinguish for sanitary purposes between waters which are obtained from comparatively shallow wells and those which are derived from wells, say, upwards of 100 ft. in depth, and sometimes reaching to the distance of more than 1000 ft. below the surface of the earth. The presumption is that waters obtained from such a depth have undergone perfect filtration through porous strata, and consequently it is not usual to view the evidence of previous contact with animal matters afforded by the presence of mineral nitrogen with so much suspicion as in the case of the waters from the shallower wells. The great efficiency of the filtration which most of these deep well waters have undergone is attested both by their freedom from organic matter, and from every kind of suspended material, whether organic or inorganic. In consequence of the excellent water obtainable from such deep wells, they have been multiplied greatly during past years, so that at the present time not only are many towns (including a part of London) and villages supplied from this source, but also nearly all larger breweries and many private establishments. In some cases these deep wells are of the kind known as 'Artesian' (from Artois, in France, where they were probably first employed); that is to say, on reaching the water-bearing stratum the water

DEEP WELL WATERS. (6th Rep. Riv. Com. p. 89.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Devonian rocks.										
Maximum . .	45·30	0·083	0·016	0·001	0·696	0·713	4·20	26·2	16·4	32·5
Minimum . .	8·94	0·021	0·005	0	0·044	0·049	1·40	0·5	3·1	3·6
Average (5 samples)	29·41	0·047	0·012	0	0·400	0·412	2·96	8·9	9·4	18·3
Polluted well at Bromyard . .	85·12	0·177	0·048	0	2·279	2·327	11·25	25·0	16·2	41·2
Polluted well at Dundee . .	27·50	0·119	0·027	0·025	0·532	0·580	3·05	9·6	8·5	18·1
From Millstone Grit.										
Well at Bradford, Yorks . . .	55·40	0·150	0·005	0·028	0·038	0·066	3·23	6·8	7·3	14·1
Well at Glossop, Derby . .	26·32	0·092	0·020	0·003	0·019	0·042	0·89	9·8	5·9	15·7
From Coal Measures.										
Maximum . .	144·88	0·198	0·064	0·170	1·468	1·494	59·85	28·2	48·5	75·0
Minimum . .	33·42	0·045	0·014	0	0	0·029	1·29	5·7	1·2	9·9
Average (9 samples)	83·10	0·119	0·034	0·044	0·207	0·278	18·05	15·1	20·6	35·7
Polluted well at Holyrood, Edinburgh . . .	92·54	0·326	0·175	0·056	0·950	1·171	7·95	27·9	8·3	36·2
From Magnesian Limestone.[1]										
Mansfield, Woodhouse . .	54·32	0·139	0·039	0	1·188	1·227	3·20	23·4	26·0	49·4
Pontefract, Yorks .	84·92	0·054	0·021	0	2·673	2·694	5·55	26·5	40·8	67·3

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[1] The following is a more recent analysis made by the writer of water derived from deep wells in the Magnesium Limestone:—

RESULTS OF ANALYSIS EXPRESSED IN PARTS PER 100,000.

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total Combined nitrogen	Chlorine	Hardness	Remarks
Sunderland and South Shields Water Supply. March 3, 1905.	45·52	0·029	0·005	Trace	0·328	0·333	3·65	35·0	Alkalinity=28·5 Ca Total lime (CaO)=1 „ magnesia (Mg = 6·30

DEEP WELL WATERS (*continued*).

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From New Red Sandstone.										
Maximum . .	62·84	0·091	0·038	0·039	3·508	3·528	7·51	19·4	20·0	35·6
Minimum . .	14·20	0	0	0	0	0·009	1·30	0	4·9	5·7
Average (28 samples)	30·63	0·036	0·014	0·003	0·717	0·734	2·94	7·4	10·5	17·9
Polluted well at Lichfield . . .	32·06	0·163	0·038	0·003	0·489	0·529	2·20	9·3	9·0	18·3
Polluted well at Liverpool . .	86·70	0·135	0·038	0·005	8·678	8·721	12·61	11·5	24·0	35·5
Polluted well at Oxton . . .	27·80	0·249	0·034	0·001	0·376	0·411	3·52	5·6	8·5	14·1
From Lias.										
Well at Northampton	57·76	0·168	0·024	0·003	0	0·026	5·15	8·6	1·7	10·3
Well at Somerton, Somerset . .	84·20	0·124	0·030	0	0·778	0·808	3·70	35·3	14·7	50·0
Polluted well at Trowbridge, Wilts .	144·34	0·236	0·057	0·002	0·550	0·609	36·70	27·4	29·7	57·1
From Oolites.										
Maximum . .	41·90	0·054	0·018	0·110	1·898	1·907	3·70	18·0	10·6	23·0
Minimum . .	26·60	0·023	0·005	0	0	0·099	1·35	8·3	3·6	18·9
Average (5 samples) .	33·60	0·037	0·010	0·022	0·625	0·654	2·69	13·8	6·8	20·6
Polluted (maximum of 3 wells) . .	71·04	0·217	0·053	0·002	0·778	0·800	7·80	26·4	12·9	39·3
Polluted (minimum of 3 wells) . .	27·48	0·106	0·020	0	0	0·047	2·10	12·6	8·6	21·2
From Hastings Sand, Lower and Upper Greensand, and Wealden.										
Maximum . .	79·20	0·120	0·021	0·074	1·074	1·085	10·00	27·8	26·0	44·3
Minimum . .	28·24	0·028	0·003	0	0	0·007	1·60	1·1	1·2	3·6
Average (20 samples)	45·20	0·068	0·014	0·016	0·196	0·223	5·38	16·8	10·5	27·3
Polluted well in Lower Greensand at Sevenoaks .	38·76	0·447	0·072	0	0·252	0·324	5·90	7·2	13·4	20·6
From Chalk.										
Maximum . .	66·34	0·131	0·064	0·029	2·277	2·319	11·10	38·6	13·8	50·0
Minimum . .	23·30	0	0	0	trace	0·014	1·00	10·8	2·7	19·1
Average (66 samples)	36·88	0·050	0·017	0·001	0·610	0·628	2·76	21·2	6·5	27·7
Polluted wells, maximum . . .	216·40	0·821	0·186	0·150	3·401	3·484	106·0	36·1	34·3	51·5
Polluted wells, minimum . . .	32·16	0·107	0·028	0	0	0·204	1·83	13·9	5·3	23·9
From Chalk beneath London Clay.										
Maximum . .	106·70	0·195	0·067	0·118	0·645	0·681	38·80	29·5	25·4	48·5
Minimum . .	33·38	0·055	0·005	0	0	0·053	2·38	0	0·9	0·9
Average (13 samples)	78·09	0·093	0·028	0·048	0·068	0·135	15·02	9·7	8·7	18·4
Polluted wells at Colchester . .	96·20	0·174	0·030	0·021	2·582	2·629	21·00	12·7	13·0	25·7
Polluted wells at Hounslow . .	82·40	0·273	0·042	0·001	0·846	0·889	9·05	26·2	8·1	34·3
From Thanet Sand and Drift.										
Maximum . .	61·10	0·133	0·021	0·190	0·438	0·457	9·10	23·7	12·0	34·0
Minimum . .	45·96	0·074	0·019	0	0	0·019	5·20	4·5	3·6	8·1
Average (4 samples) .	53·84	0·113	0·020	0·072	0·116	0·202	6·32	14·4	7·6	22·0

rises to the level or even considerably above the level of the ground, due to the underground water being confined under pressure beneath an impervious stratum of clay or the like, and through the outcrop of the water-bearing stratum being at a considerably higher altitude than the point at which the boring has been made. Thus, in the London basin, 'Artesian wells' are obtained by sinking through the London clay into the chalk beneath, which has its outcrop at considerable altitudes in the chalk hills on the north and south of the Thames valley. Owing to the large abstraction from such water-bearing strata, the water of many wells which formerly rose to the surface has now to be pumped. In the majority of deep wells the water does not rise nearly to the surface, and the pumps have often to be placed at considerable depths in the shaft. It is usual to line these wells with closely-fitting iron cylinders, in order to exclude surface water, as unless this is done the deep wells may become as objectionable and dangerous as shallow ones.

The preceding tables afford a survey of the general character of the deep well waters obtained in Great Britain. In nearly all the samples of which the maximum, minimum, and average results are given, it may be taken that the wells were unpolluted by surface water, but for the sake of comparison there are appended to most of the sections analyses of deep well waters from the same strata in which pollution by surface or imperfectly-filtered water is highly probable.

These results demonstrate the great superiority from a chemical point of view of the subterranean waters obtained at great depths to those derived from shallow wells. Indeed, these deep well waters are, as regards organic matter, amongst the purest to be found in nature, and hence, unless extremely hard, are of the best quality for drinking purposes.

Closely associated with these deep well waters is the next group of spring waters.

6. *Spring water.* In the following table is given the composition of, presumably unpolluted, British spring waters arranged according to the geological nature of the ground from which they are derived, whilst for the sake of comparison the composition of probably polluted spring waters from the same geological source is in many cases appended.

7. *Mineral spring waters.* Many spring waters possess marked medicinal properties in consequence of the materials they hold in solution. Until the discovery of radium it was generally supposed by chemists that the therapeutic value of such waters containing only an insignificant amount of mineral matter must be imaginary, but it is now known that some of these, such as the waters of Bath and Buxton, are pronouncedly radioactive, and it is generally accepted at the present time that the old-established efficacy of these waters in the treatment of gout and rheumatism is due to their content of radioactive material (*see* Nature, 1911, 86, 157). Indeed, radium-salt is now much employed for the artificial production of radioactive water for medicinal purposes. An immense number of mineral waters are in use, and have been submitted to careful analysis; a very extensive collection of such analyses is to be found in Raspe's Heilquellen Analyse, Dresden, 1885.

These mineral waters are conveniently classified by Hermann Weber (Quain's Dictionary of Medicine), according to the ingredients which characterise them, into—(1) Simple thermal waters; (2) common salt or muriated saline waters; (3) alkaline waters; (4) sulphated saline waters; (5) iron or chalybeate waters; (6) sulphur waters; (7) earthy and calcareous waters.

(1) *The simple thermal waters*, whilst containing only a moderate proportion of dissolved solids, are characterised by a high temperature, from 27°–65°, and sometimes by the presence of an unusually large proportion of nitrogen, which is now known to be mixed with appreciable quantities of helium. Doubtless the medicinal reputation of most, if not all, of these waters depends on their radioactivity. The principal springs of this class are: Panticosa, Leukerbad, Bormio, Gastein, Pfäffers, Johannisbad, Ragatz, Wildbad, Plombières, Buxton, Bath, Lucca, Teplitz, Schlangenbad, &c.

(2) *Common salt or muriated saline waters* contain sodium chloride as the principal constituent, although this also occurs often in large quantity in many of the other classes of mineral waters. These salt waters or brines are very common in almost all countries. Some of the principal ones in England are: Droitwich, Nantwich, Middlewich, Woodhall, and Harrogate; Leamington and Cheltenham along with sodium sulphate. In Germany: Kissingen, Homburg, Nauheim, Kreuznach, Soden, Pyrmont, Wiesbaden, Ischl, Kreuth, Baden-Baden, &c. In France: Bourbonne-les-Bains, Lamotte-les-Bains, Balaruc, Salins. In Italy: Castellamare, Ischia, Monte Catini, La Porretta. In Switzerland: Bex.

(3) *Alkaline waters* are characterised by the presence of sodium carbonate, almost always with more or less free carbon dioxide, and sometimes with a large quantity also of sodium chloride. Of the simply alkaline waters, there are—(*a*) *Hot*: Vichy, Neuenahr, Mont-Dore, Chaudesaigues, Néris; (*b*) *Cold*: Apollinaris, Vals, Salzbrunn, Bilin, Wilhelmsquelle, Taunus, Marcolo; whilst the chief muriated alkaline waters are: (*a*) *Hot*: Ems, Royat, La Bourboule; and (*b*) *Cold*: Luhatschowitz, Selters, Gleichenberg, Rosbach, Vic-sur-Cere. Several of these, but especially La Bourboule and Mont Dore, contain a marked proportion of arsenic.

(4) *Sulphated waters* contain either sodium or magnesium sulphate, or both, as the prominent ingredients, in some cases also associated with sodium carbonate and chloride. They are often called '*bitter waters*.' The chief simple sulphated waters are: Galthof, Pullna, Saidschutz, Sedlitz, Birmensdorf, Ivanda, Hunyadi Janos, Epsom, Aranjuez, Friedrichshall, Mergentheim; the two latter are also rich in chlorides. Weaker springs of the same kind are found at Leamington, Cheltenham, Scarborough, and at Purton Spa. Of alkaline sulphated waters there are: Carlsbad, Marienbad, Tarasp-Schuls, Franzensbad, Elster, and Bertrich.

(5) *Iron or chalybeate waters* are those in which an unusual proportion of this element is present, either in otherwise comparatively pure water or associated with other mineral matter

SPRING WATER. (6th Rep. Riv. Com. p. 107.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Granite and Gneiss.										
Maximum . .	9·44	0·119	0·019	0·002	0·204	0·210	3·10	1·2	5·3	5·6
Minimum . .	1·40	0	0	0	0	0·013	0·55	0	1·2	1·2
Average (8 samples) .	5·94	0·042	0·008	0·001	0·106	0·115	1·69	0·4	2·6	3·0
From Silurian Rocks.										
Maximum . .	27·10	0·096	0·042	0·005	0·659	0·674	3·70	6·9	9·3	15·8
Minimum . .	3·04	0·011	0·002	0	0	0·011	0·90	0	1·5	1·5
Average (15 samples)	12·33	0·051	0·014	0·001	0·178	0·192	1·84	1·5	5·3	6·8
From Devonian and Old Red Sandstone.										
Maximum . .	66·90	0·124	0·034	0·006	4·104	4·128	13·80	22·4	12·4	29·9
Minimum . .	5·50	0·009	0·001	0	0·013	0·028	1·30	0	1·9	2·2
Average (22 samples)	25·06	0·054	0·012	0·001	0·764	0·777	3·85	4·8	7·2	12·0
From Mountain Limestone.										
Maximum . .	98·50[1]	0·286	0·023	0·006	1·022	1·036	32·00[1]	20·9	29·5	48·5[1]
Minimum . .	15·70	0·011	0	0	0	0·001	0·70	2·1	3·3	11·0
Average (13 samples)	32·06	0·087	0·010	0·001	0·224	0·235	4·63	10·9	8·9	19·8
From Yoredale and Millstone Grits.										
Maximum . .	40·80	0·109	0·028	0·006	0·617	0·650	3·45	21·4	11·5	26·4
Minimum . .	3·32	0·017	0·004	0	0	0·005	0·95	0	2·7	2·7
Average (8 samples) .	17·73	0·042	0·011	0·001	0·169	0·181	1·73	6·6	5·7	12·3
From Coal Measures.										
Maximum . .	39·60	0·120	0·027	0·008	1·813	1·860	3·35	14·5	17·1	25·7
Minimum . .	6·84	0·029	0·004	0	0	0·010	0·95	0	2·3	2·6
Average (22 samples from millstone grit and coal measures) . . .	21·91	0·050	0·014	0·001	0·393	0·408	1·85	5·2	7·9	13·1
From Magnesian Limestone.										
Pontefract, Yorks .	66·52	0·058	0·038	0·002	1·686	1·726	3·40	4·9	34·8	59·7
From New Red Sandstone.										
Maximum . .	74·26	0·118	0·069	0·014	1·256	1·275	7·00	19·8	25·0	35·7
Minimum . .	12·90	0·027	0	0	0	0·006	1·30	0	4·2	8·0
Average (15 samples)	28·69	0·065	0·017	0·001	0·330	0·349	2·19	8·1	10·7	18·8
From Lias.										
Maximum . .	58·12	0·131	0·036	0·009	1·332	1·353	4·80	32·3	17·4	45·7
Minimum . .	21·22	0·024	0·006	0	0	0·035	1·35	9·1	5·3	15·1
Average (7 samples) .	36·41	0·073	0·019	0·001	0·467	0·487	2·48	21·3	8·8	30·1
From Oolites.										
Maximum . .	52·16	0·140	0·021	0·014	1·157	1·168	3·30	30·0	13·5	38·7
Minimum . .	22·30	0·009	0·003	0	0	0·014	0·97	11·3	3·5	16·9
Average (35 samples)	30·33	0·043	0·011	0·001	0·402	0·414	1·55	18·2	6·2	24·5
From Lower Greensand, Hastings Sand, and Upper Greensand.										
Maximum . .	68·40	0·135	0·028	0·003	1·116	1·129	7·10	25·0	22·1	40·2
Minimum . .	4·55	0·002	0·002	0	0·034	0·045	1·10	0	0·7	0·7
Average (19 samples)	30·05	0·053	0·012	0	0·326	0·338	2·98	13·6	6·6	20·2
From Chalk.										
Maximum . .	39·30	0·097	0·023	0·006	0·863	0·874	7·40	25·3	8·1	32·2
Minimum . .	25·36	0·008	0·003	0	0	0·009	1·05	6·8	3·6	12·4
Average (30 samples)	29·84	0·044	0·010	0·001	0·382	0·392	2·45	18·1	5·5	23·6
From Fluvio Marine, Red Crag, Drift, and Gravel.										
Maximum . .	225·24	0·164	0·043	0·007	1·277	1·293	4·27	32·2	94·3	126·5
Minimum . .	24·62	0·004	0·006	0	0·004	0·034	2·10	0·7	6·1	12·6
Average (10 samples)	61·32	0·086	0·019	0·001	0·354	0·374	2·76	18·0	19·6	37·6

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[1] Water supply of Weston-super-Mare; these exceptionally high results doubtless due to access of sea water.

Thus, of comparatively pure chalybeate waters, there are those of Schwalbach, Spa, Brückenau, Schandau, Liebwerda, Flinsberg, Freienwalde, Recoaro, Königswarth, Liebenstein, Altwasser, Alexisbad, Muskau, Tunbridge Wells, and some of the springs at Harrogate; whilst of waters in which the iron is associated with a considerable quantity of other salts, there are those of Aratapak, Orezza, Pyrmont, Driburg, Rippoldsau, Griesbach, Antogost, Petersthal, Bocklet, St. Moritz, Reinerz, Godesberg, Cudowa, Imnan, and Santa Catarina.

(6) *Sulphur waters* are those containing appreciable quantities of either sulphuretted hydrogen or the sulphides of sodium, potassium, calcium, or magnesium. Some of the more important thermal sulphur waters are those of Eaux Chaudes, Cauterets, Saint Sauveur, Barèges, Bagnères-de-Luchon, Ax, Escaldes, Le Vernet, Amélie-les-Bains, Uriage, Allevard, Aix-les-Bains, Aix-la-Chapelle, Baden (Austria), Baden (Switzerland), Lavey, Schinznach, Battaglia and Abano in the Euganean Mountains, Panticosa, Mehadia, Helouan, near Cairo; whilst of cold sulphur springs there are those of Eilsen, Neundorf, Langenbrücken, Weilbach, Meinberg, Reutlingen, Enghien, Challes, Stachelberg, Heustrich, Gurnigel, some of the Harrogate springs, Llandrindod, Builth, Moffat, Strathpeffer, Lisdunvarna.

(7) *Earthy and calcareous waters* are characterised by the presence of large proportions of calcium carbonate and sulphate, and magnesium carbonate. Some of the more important are found at Wildungen, Lippspringe, Weissenburg, Contrexéville, Bagnères-de-Bigorre, St. Arnaud, Crausac, whilst the table waters of Couzan, St. Galmier, and Taunus are of the same character.

8. *Sea water.* The ocean is a great evaporating-basin, which is constantly receiving waters, more or less impure, in the shape of rivers, whilst at the same time it is constantly losing pure water in the form of vapour, the impurities remaining behind and imparting to the sea its well-known saline character. This also distinguishes all lakes which are devoid of outlet, like the Dead Sea, Caspian, Aral, Great Salt Lake, Utah, &c., in which the same process of concentration by evaporation is going on. As will be seen from the table on the next page, the composition of the ocean varies considerably in different places and at different depths, whilst land-locked seas, like the Mediterranean, Black Sea, and Baltic, present even still greater differences.

Thus in the vicinity of the poles the proportion of salt is less than near the equator; similarly, land-locked seas, such as the Black Sea and Baltic, which receive large rivers are less salt; whilst the Mediterranean in most places is more salt than the great oceans. Of salt lakes the Dead Sea is far more and the Caspian far less salt than the oceans. In addition to sodium chloride, the principal substances present in sea water are the sulphates and carbonates of calcium and magnesium, and salts of potassium, whilst in very minute quantities there are found also a number of others, amongst which may be mentioned bromides, iodides and fluorides, silica, phosphoric and nitric acids, iron, silver, gold, copper, lead, arsenic, zinc, cobalt, nickel, lithium, rubidium, and caesium.

The volume of gas dissolved in sea water is, according to Hunter (Chem. Soc. Trans. 187, 20), only from 2·2 to 3·5 vols. in 100 vols. of water.

	CO_2 per cent.	O per cent.	N per cent.
2·2 vols. consisted of	28·62	49·44	21·94
3·5 ,, ,,	48·28	17·22	34·50

A very extensive observation of the composition of sea water was made in connection with the voyage of H.M.S. *Challenger*, and the elaborate report prepared thereon by Dittmar should be consulted for detailed information on this subject. From 77 complete analyses, the following numbers for the average composition of ocean-water salts are calculated:—

Average composition of ocean-water salts, in parts per 00 of total salts (Dittmar).

Chlorine	55·292
Bromine	0·1884
Sulphuric acid (SO_3)	6·410
Carbonic acid (CO_2)	0·152
Lime (CaO)	1·676
Magnesia (MgO)	6·209
Potash (K_2O)	1·332
Soda (Na_2O)	41·234
(Basic oxygen equivalent to the halogens)	(−12·493)
	100·000

The salinity of the ocean, expressed in parts of total salts per 1000 parts of sea-water, was found to vary between the following limits: Minimum (from the southern part of the Indian Ocean, south of 66° lat.), 33·01; maximum (from the middle of the North Atlantic, at about 23° lat.), 37·37.

As regards the carbon dioxide in sea water, Dittmar comes to the following conclusions: (1) Free carbonic acid in sea water is the exception; as a rule, the carbonic acid is less than the proportion corresponding to bicarbonate. (2) In surface waters the proportion of carbonic acid increases when the temperature falls, and *vice versâ*. (3) Within equal ranges of temperature it seems to be lower in the surface water of the Pacific than it is in the surface water of the Atlantic Ocean.

Drinking water. As has long been known, the palate is by no means a safe guide in the choice of drinking water, for although unpalatable waters are obviously unsuitable for drinking, palatable waters may contain materials capable of doing serious injury. It is now established beyond question that the diseases termed 'zymotic' are due to minute forms of life known as micro-organisms, and in a number of cases the specific forms responsible for such diseases have been discovered, identified, and studied. Of zymotic diseases there are two—Asiatic Cholera and Typhoid Fever—which are with certainty known to be propagated by drinking water, and in the case of these two diseases authorities are agreed as to the particular organisms to which they are due. The propagation unquestionably takes place through the excreta of persons suffering from these diseases gaining access to water which is afterwards used for drinking, whilst water contaminated with the sewage of healthy persons is generally believed to be capable of producing

(Results of Analysis expressed in parts per 1000.)

Seas	Point of collection of sample	Na	Cl	Mg	Ca	K	SO_4	Br	Co_3	Fe	Fixed Residue	Authors
Atlantic Ocean	0° 47′ S.—33° 20′ W.	11·081	19·460	0·9568	0·4567	0·7604	2·577	0·4069	—	—	35·700	Bibra, Annalen, 77, 90.
”	20° 54′ N.—40° 44′ W.	10·464	19·012	1·2735	0·4684	0·7252	2·446	0·3102	—	—	34·700	
”	41° 18′ N.—36° 28′ W.	11·719	20·840	1·1981	0·5568	0·6682	3·029	0·3878	—	—	38·400	
”	Cape Horn	10·457	18·841	1·1763	0·5289	0·5916	2·878	0·3271	—	—	34·800	
North Sea	. . . . . .	10·117	18·954	1·3141	0·4782	0·6811	2·563	0·2924	—	—	34·400	
”	Between Belgium and England	10·206	18·168	1·1582	0·3244	0·3536	2·590	(?)	—	—	32·800	Bischof, C. Géolog., 1, 99.
Straits of Dover	Some miles from Havre	10·142	17·794	1·2305	0·4093	0·0425	2·882	0·1046	0·078	traces	32·700	Figuier et Mialhe, J. Pharm. [iii.] 13, 406.
Mediterranean	Marseilles	10·688	21·099	3·0037	0·048	0·0041	5·716	(?)	0·142	—	40·700	Laurent, J. Pharm. 21, 93. [ii.] 92, 172.
”	At 3500 metres from the coast of Cette	11·706	20·527	1·3104	0·4411	0·2643	2·943	0·434	0·0679	0·0028	37·700	Usiglio, Ann. Chim. Phys.
”	The Lagunes of Venice	8·779	15·882	1·1646	0·1769	0·4356	2·662	(?)	—	—	29·100	Calamai, 1847.
Pacific Ocean	3·5 metres below the surface	10·262	18·950	1·3151	0·4719	0·6038	2·786	0·3102	—	—	34·700	Bibra, *l.c.*
”	140 metres below the surface	10·233	19·321	1·4714	0·4752	0·6336	2·827	0·2394	—	—	35·200	
Baltic	. . . . . .	5·894	10·386	1·6115	0·0365	—	0·719	—	—	—	17·710	Pfaff, Schweigger's Journ. 22, 271.
Black Sea	Coast south of the Crimea	5·512	9·574	0·6622	0·1305	0·0975	1·2505	0·005	0·2475	0·1271	17·605	Göbel, P. Suppl., 1, 187.
Sea of Azof	Between Kertch and Mariapol	3·997	6·585	0·4010	0·0908	0·0670	0·8045	0·004	0·0695	0·0358	11·900	*Ibid.*
Caspian Sea	South west of Pischnoï	1·144	2·737	0·4098	0·1916	0·1397	1·337	(?)	0·0773	0·0401	6·296	*Ibid.*
Dead Sea	From the surface	0·885	17·628	4·177	2·150	0·474	0·2424	0·167	traces	traces	27·078	Terreil, Compt. rend. 62, 1329. (Wurtz, Dictionnaire de Chimie.)
”	From 300 metres below the surface	14·300	174·985	41·428	17·269	4·386	0·6276	7·093	traces	traces	278·135	

To these may be added the following analysis of the water of the Irish Channel in the winter of 1870 (Thorpe and Morton, Chem. Soc. Trans. 1871, 506).

(Results of Analysis expressed in parts per 1000.)

NaCl	26·43918	$MgSO_4$	2·06608	$CaSO_4$	1·33158	NH_4Cl	0·00044	Sp.gr. at 0°C. = 1·02721
KCl	0·74619	$MgCO_3$	Trace	$CaCO_3$	0·04754	$FeCO_3$	0·00503	” ” 15°C. = 1·02484
$MgCl_2$	3·15083	$Mg(NO_3)_2$	0·00207	LiCl	Trace	SiO_2	Trace	Total = 33·85946
$MgBr_2$	0·07052							

diarrhœa and other minor disturbances in those drinking it.

In selecting water for drinking purposes it is necessary, therefore, in the first instance, to make a careful inquiry as to the possibility of the water having been in contact with refuse animal matters, and if possible all waters open to such suspicion should be discarded. For the same reason it is of the first importance in the examination of water to discover what evidence, if any, there is of the water having been in contact with such refuse substances. In the present state of knowledge this is a difficult matter, as, although the results of chemical analysis frequently point to such contamination when on a sufficiently large scale, it is occasionally and indeed generally impossible to prove the negative. The bacteriological examination, on the other hand, is of extreme delicacy, but, inasmuch as we have at present no means of ascertaining whether the bacteria indicative of fæcal contamination are derived from man or from the lower animals, the results obtained by this means also are often of restricted value from a hygienic point of view. It becomes, therefore, of the greater importance to make a thorough inspection of the source and to trace out the further history of the water, for unless this be done the results of the scientific examination may often receive an erroneous interpretation. As, however, it is comparatively rarely that natural waters are to be met with which are absolutely above suspicion of *any* contamination with refuse animal matters, it is generally necessary to be satisfied with relative purity, and thus the examination, chemical and biological, of drinking waters becomes a matter of the highest importance and utility. The natural waters which can lay claim to the greatest degree of safety for drinking purposes are of two kinds.

1. Unpolluted surface waters (generally upland waters).
2. Naturally filtered waters (spring and deep well waters).

In the first case the waters, both by inspection and analysis, must bear no evidence of animal contamination, and this is generally only possible in the case of waters which are found at altitudes above that of human habitations. A number of our large towns are supplied with water of this kind, although the gathering-grounds do in most cases contain some houses, so that absolute freedom from sewage contamination cannot generally be guaranteed. In the table on p. 697 the chemical composition of some of these upland surface water supplies is recorded.

The majority of upland surface waters are either very soft or of only very moderate hardness, and as in many of these towns extensive manufactures are carried on, these supplies are not only valued because of their safety for drinking, but also on account of their fitness for industrial purposes. It should always be remembered, however, that these surface waters may at times receive more or less sewage contamination, and that the ova of animal parasites derived from the cattle grazing on the gathering-grounds may also be present, and that, therefore, to reduce these sources of danger to a minimum, it is highly desirable that such waters should be subjected to prolonged storage in reservoirs, followed by careful filtration through sand before delivery to the consumer.

In the second class of water its original purity is a matter of secondary consequence, the guarantee of safety resting upon the exhaustive process of filtration which the water has undergone in passing through porous strata of the earth's crust. This filtration effects, on the one hand, the more or less complete chemical purification of the water from organic substances, and on the other hand the mechanical removal of organised matters, such as bacteria and animal parasites. The most perfectly-filtered waters of this kind are those obtained from springs and from deep wells, and, again, many of our towns are supplied with water of this kind—more especially from the chalk, greensand, Oolite, and New Red Sandstone formations, which constitute efficient filter beds. In the table on p. 698 is recorded the chemical composition of the water supplied to some of our towns from such sources.

Of other forms of drinking water we have river waters and shallow-well waters, upon both of which a very large portion of the population is dependent for domestic supply. Both of these classes of water are open to grave objections, and nearly all the best authenticated cases of the propagation of cholera and typhoid through drinking water have been traced to shallow wells. There are, however, many potent influences tending to remove bacteria from water which, on *a priori* reasoning, would have been regarded as almost, if not wholly, inoperative. These causes are mainly the process of devitalisation which pathogenic bacteria undergo in natural, and more especially in surface waters, and the resistance offered by even a comparatively small thickness of soil or other porous material to the passage of micro-organisms. But although these causes are to be looked upon as tending to keep the evils which can result from contaminated drinking water within narrower limits than might have been anticipated, still the possibility of their failure must be constantly kept in view, and they must not be allowed to check the endeavour to substitute unimpeachable for suspicious sources of supply.

Every effort should be made to exclude avoidable sources of contamination, to select the best water which the source affords, and to submit it to the most effective purification available. The improvements which can thus be brought about in water supplies obtained from suspicious sources is conspicuously exemplified in the case of the London supply derived from the rivers Thames and Lea. Here, on the one hand, increasing vigilance has been exercised by the Thames and Lea Conservancy Boards in the exclusion of dangerous matters from the rivers and their tributaries, whilst on the other hand the authorities supplying water have removed their intakes to points on these streams above the most serious pollutions; by increasing their storage capacity they are enabled not only to avoid drawing from the rivers in times of flood, but also to bring about a great amelioration in the quality of the water during its sojourn in the reservoirs, whilst by improving their filtering appliances they secure a more perfect purification

UPLAND SURFACE WATER SUPPLIES.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness			Remarks
								Temporary	Permanent	Total	
Heywood and Middleton supply, Sep., 1908	8·96	0·044	0·010	0	0·037	0·047	1·15	0·4	2·2	2·6	Almost clear.
Torquay supply, April, 1903	6·84	0·141	0·018	Trace	0·118	0·136	1·50	0·3	2·2	2·5	Very slightly turbid.
Paisley supply, Sep., 1898	8·68	0·487	0·064	0·002	0·035	0·101	1·15	0·1	3·8	3·9	Clear.
Pontypridd supply, Nov., 1907	5·28	0·183	0·025	0	0·032	0·057	0·80			2·3	Very slightly turbid.
Cardiff supply, Dec., 1908	6·28	0·160	0·016	0	0·024	0·040	0·75	0·3	3·0	3·3	Almost clear.
Aberdeen supply, intake from River Dee, March, 1910	4·76	0·193	0·026	0	0·010	0·036	0·90	0·2	1·6	1·8	Very slightly turbid.
Aberdeen, proposed supply from River Avon, March, 1910	2·60	0·091	0·015	0	0·008	0·023	0·55	0	0·5	0·5	Very slightly turbid.
Glasgow, L. Katrine water, Nov., 1891.	2·80	0·149	0·025	0	0·004	0·029	0·72	—	—	0·6	Slightly turbid.
Liverpool, Rivington Water, Average for 1903	9·82	0·153	0·025	0·002	0·005	0·032	1·52			4·1	
,, Vyrnwy Water ,,	4·67	0·211	0·027	0·002	0	0·029	0·87			1·5	
Birmingham, Elan Valley Water, Jan., 1911	6·44	0·171	0·019	0	0·016	0·035	0·90	0·2	2·5	2·7	Almost clear.
,, ,, ,, June, ,,	4·92	0·089	0·015	Trace	0·016	0·031	0·85	0·3	2·6	2·9	Almost clear.
Dewsbury supply, Dec., 1910	7·52	0·226	0·025	0·002	0·053	0·080	1·00	0·2	2·7	2·9	Slightly turbid and opalescent.
,, ,, July, 1911	6·24	0·067	0·005	Trace	0·035	0·040	1·10	0·2	2·5	2·7	Slightly turbid.
Belfast, Woodburn supply, Jan., 1910	14·40	0·325	0·022	Trace	0·032	0·054	1·75	5·5	3·6	9·1	Almost clear.
,, ,, ,, June, ,,	15·32	0·155	0·019	Trace	0·027	0·046	1·50	5·6	3·4	9·0	Almost clear.
,, Stonyford supply, Jan., 1910	13·68	0·427	0·036	0	0·026	0·062	1·20	4·4	3·5	7·9	Almost clear.
,, ,, ,, June, ,,	12·16	0·265	0·031	Trace	0·016	0·047	1·15	4·2	3·4	7·6	Almost clear.
,, Mourne Mountains supply, Jan., 1910	9·28	0·195	0·015	0	0·041	0·056	1·25	0·2	3·4	3·6	Very slightly turbid.
,, ,, ,, ,, June, ,,	7·00	0·171	0·018	Trace	0·027	0·045	1·25	0·5	2·2	2·7	Slightly turbid.

WATER SUPPLIES FROM DEEP WELLS AND SPRINGS.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Am-monia	Nitrogen as nitrates and nitrites	Total com-bined nitrogen	Chlor-ine	Hardness			Remarks
								Tempo-rary	Perma-nent	Total	
Portsmouth supply: from chalk springs, August, 1905 .	29·80	0·032	0·009	Trace	0·326	0·335	1·65	19·0	5·3	24·3	Very slightly turbid.
Nottingham: borehole 500 ft. deep in New Red Sandstone, Dec., 1910	19·80	0·020	0·005	0	0·020	0·025	1·25	9·6	7·8	17·4	Almost clear.
Liverpool: Dudlow Lane well in New Red Sandstone, 1903	18·43	0·024	0·007	0	0·677	0·684	3·01			7·8	
„ Green Lane well „ „ „ „	32·79	0·028	0·007	0	0·625	0·632	3·33			19·1	
„ Windsor well „ „ „ „	41·20	0·019	0·006	0	0·786	0·792	4·38			26·5	
Long Eaton supply: well in New Red Sandstone, Sep., 1911	48·32	0·038	0·008	0·002	0·295	0·305	2·50	22·3	13·4	35·7	Very slightly turbid.
Eastbourne supply: well in chalk, August, 1911 . .	28·56	0·028	0·004	0	0·378	0·382	3·63	15·1	3·8	18·9	Clear.
Lancaster: well 260 ft. deep in Grey Sandstone, Sep. 1901	22·00	0·016	0·004	Trace	Trace	0·004	2·20	9·8	5·9	15·7	Very slightly turbid.
Mansfield: well in New Red Sandstone, May, 1907 . .	14·92	0·034	0·006	Trace	0·373	0·379	1·30	0·6	8·0	8·6	Almost clear.
E. Worcestershire Waterworks; Barcot well in New Red Sandstone, Oct., 1908	17·72	0·028	0·006	Trace	0·314	0·320	1·20	2·1	7·0	9·1	Almost clear.
Shanklin: springs in Upper Greensand, June, 1908 . .	34·88	0·036	0·009	0	0·276	0·285	3·40	18·6	5·3	23·9	Almost clear.
Exmouth: borehole 338 ft. deep in New Red Sandstone, June, 1909	23·60	0·025	0·006	0	0·386	0·392	2·60	9·1	4·6	13·7	Almost clear.
Great Grimsby: well in chalk at Healing, April, 1911 .	30·00	0·010	0·005	0	0·386	0·391	1·80	18·6	3·6	22·2	Almost clear.
„ „ „ at Cleethorpes, April, 1911 . .	31·00	0·011	0·004	0	0·149	0·153	2·88	19·4	3·5	22·9	Almost clear.

of the water which they have abstracted. Thus the water supplied to London to-day is both chemically and hygienically very different from what it was 60 years ago, although still derived from the same streams, which in the ordinary course of events would be more polluted now than they were then.

Importance to be attributed to various ingredients of drinking water. It is only possible here to give a brief account of the importance which is usually attributed to the several ingredients which are commonly determined in the analysis of drinking waters.

Dissolved gases. The gases present in ordinary drinking waters are those of the atmosphere—oxygen, nitrogen, and carbon dioxide. Their quantitative determination is of little or no significance in connection with the quality of the water for drinking, excepting that through the absence of dissolved gases a water has the flat taste of that which has been recently boiled. It is sometimes supposed that the absence of a due proportion of dissolved oxygen in water is an indication of the presence of decomposing organic substances, but this can only be the case with surface waters, as the very purest subterranean waters are almost entirely destitute of it. In the following table the proportion of the several dissolved gases in different kinds of water is recorded :—

Gases dissolved in 100 cub. ins. of water	Rain-water	Cumberland mountain water	Loch Katrine water	Thames water	Deep chalk well water
	cub. ins.	cub. ins.	cub. ins.	cub. ins.	cub. ins.
Oxygen	1·308	1·424	1·731	1·325	1·944
Nitrogen	0·637	0·726	0·704	0·588	0·028
Carbon dioxide . . .	0·128	0·281	0·113	4·021	5·520
	2·073	2·431	2·548	5·934	7·492

The large proportion of dissolved carbon dioxide in the Thames and deep chalk well water is mainly combined with calcium carbonate as bicarbonate.

Total solid residue. It is only rarely that the amount of the residue left by a water on evaporation affords any evidence of its fitness for drinking. As a general rule, it may be stated that waters which contain very small residues are probably pure and unpolluted, but on the other hand many waters of organic purity contain large proportions of mineral matter in solution. It is impossible to assign limits to the proportion of mineral matter which may be present in water without interfering with its fitness for drinking, more especially as opinion is divided as to the influence of the several constituents on health (*v.* also *Hardness of water*). Nearly all the best drinking waters in the United Kingdom yield less than 50 parts of solid residue per 100,000, and most of them very considerably less. The use of waters yielding much larger residues is generally excluded by the inconvenience which attends their employment for general domestic purposes, in consequence of their unfitness for boilers and washing.

Organic matter. As will be pointed out (under *Water analysis*), the accurate determination of the organic matter in water is attended with great difficulties, and none of the methods of analysis in use claims to effect more than a partial determination. Thus in the 'combustion process' the organic carbon and nitrogen are determined with more or less accuracy; in the alkaline permanganate process that portion of the organic nitrogen is discovered which is readily convertible into ammonia; whilst in the 'permanganate' or 'oxygen' process the proportion of permanganate destroyed by the organic matter is taken into account. Although it may be stated generally that the smaller the proportion of organic matter the more desirable is the water for drinking, still of greater importance is the determination of the origin of the organic matter present, whether animal or vegetable. The presence of vegetable matter is of comparatively little consequence, more especially as even small amounts interfere with the palatability of the water, what is known as a 'peaty taste' being imparted by any amount yielding much in excess of 0·2 part per 100,000 of organic carbon. Sometimes much light may be thrown on the origin of the organic matter in water by the proportion which the carbon and nitrogen exhibit towards each other, especially when this is considered in connection with the proportions of ammonia, nitrates, nitrites, and chlorine. Inasmuch as animal matter in general contains a much higher proportion of nitrogen to carbon than does vegetable matter, it follows that the higher the ratio of nitrogen to carbon in the organic matter present in a sample of water, the more probability is there, *cæteris paribus*, of its being derived from animal sources and *vice versâ*. The possibility of such diagnosis, however, is considerably limited by the fact that in the oxidation of peaty matter the organic carbon disappears much more rapidly than the nitrogen; whilst, on the other hand, in the oxidation of animal matter there is conversely a tendency for the organic carbon to become concentrated, thus leading to a simulation of animal matter in the case of vegetable, and a simulation of vegetable matter in the case of animal substances after oxidation.

It is thus essential that the evidence afforded by the proportion of organic carbon to nitrogen should be supplemented by an inspection of the source, and by a consideration of the mineral nitrogenous ingredients—ammonia, nitrates, and nitrites—all of which are principally derived from the decomposition of animal matters.

Albuminoid ammonia. The ammonia yielded on distillation with alkaline permanganate is so frequently made the only measure of the organic matter present in water that a few words are necessary to indicate what is the importance to be attached to the results obtained in this simple process. According to its author, the late Mr. Wanklyn, 'deep spring water is often so pure as not to yield 0·01 part of albuminoid ammonia per million; and unless mixed with surface water does not yield so much as 0·05 part.' 'The filtered water supplied by water companies—no matter whether derived from a lake, from clean mountain streams, or from defiled rivers—yields from 0·05 to 0·10 part of albuminoid ammonia per million; and, indeed, if the filtration be efficient, approximates to 0·05.' 'When the filters are over-taxed, as happens in the rainy season and in the winter, water companies supply imperfectly-filtered water, in which as much as from 0·10 to 0·20 part of albuminoid ammonia is found.' This statement must be accepted with great reserve, for in the winter months such surface waters almost invariably contain a much larger proportion of organic matter than during the dry season, thus accounting for the increase in albuminoid ammonia quite irrespective of any over-taxing of the filters. On the other hand, the albuminoid ammonia is the chemical ingredient in water which is most affected by filtration. It would appear, therefore, that suspended particles of vegetable and animal matter, which are removed by sand filtration, are particularly productive of ammonia on distillation with alkaline permanganate. In fact, the *chemical* difference between a water before and after sand filtration is often only attested by the diminished proportion of albuminoid ammonia yielded by the filtered water.

Oxygen, or permanganate process. The analytical value of measuring the proportion of organic matter in water by the amount of permanganate it is capable of decolorising is discussed in the section of this article on *Water analysis*, and it will be sufficient here to give some idea of how the results are to be interpreted. As in the case of the organic elements determined by combustion, it has here again been attempted to establish a scale of classification, which, however, must also be used with the greatest caution and in conjunction with the other analytical data, as well as with regard to the water's source and history. Thus the following artificial standards have been suggested:—

—	Oxygen absorbed in three hours at room temperature from potassium permanganate by 100,000 parts of water	
	For Upland Surface Water	For other Water
Class I. Water of great organic purity . .	0–0·1 part	0–0·05 part
„ II. „ medium „ . .	0·1–0·3 „	0·05–0·15 „
„ III. „ doubtful „ . .	0·3–0·4 „	0·15–0·2 „
„ IV. Impure water	above 0·4 „	above 0·2 „

It will be readily understood that a great drawback to this permanganate process consists in its not distinguishing between nitrogenous and non-nitrogenous organic matter. Hence it is very desirable that, if the combustion process cannot be resorted to, it should be supplemented by a determination of the 'albuminoid ammonia,' or of the Kjeldahl nitrogen (*see* p. 719).

Mineral nitrogen (ammonia, nitrates, and nitrites). The importance of these ingredients is an indirect one. In themselves they in no way influence the wholesomeness of drinking water; but, on the other hand, they are of consequence as indicating what the previous history of the water has been. Thus, in the ordinary process of decomposition to which organic matters are subjected in nature, the nitrogen is principally liberated in the form of ammonia, and this, by subsequent fermentative oxidation, may become converted into nitrites and nitrates. Moreover, owing to the far greater average richness in nitrogen of animal over vegetable matters, it is evident that these primary and secondary products of decomposition furnish valuable evidence as to the previous contact of water with nitrogenous, and more especially animal, substances. As a general rule, the presence of ammonia indicates a more recent contact with such matters than does that of nitrates or nitrites, although in the case of ome deep subterranean waters it appears that the nitrates originally present in the water have undergone reduction to ammonia, and hence the latter in such cases must be regarded as evidence of a more remote character even than the nitrates themselves. Again, in the ordinary course of nitrification in nature the ammonia is wholly converted into nitrate, the preliminary oxidation to nitrite being rapidly passed over; but if water containing nitrates is brought in contact with organic matter, these nitrates become more or less reduced to nitrites through the agency of certain micro-organisms (P. F. Frankland, Chem. Soc. Trans. 1888, 373; Warington, *ibid.* 742), and hence the presence of nitrites generally constitutes evidence of contamination with organic matter subsequent to the original nitrification, rather than to the latter having been imperfect. The fact must also not be lost sight of that nitrates can be reduced by certain microbes in the presence of organic matter with elimination of the nitric nitrogen in the free state, or as oxides of nitrogen, and that a contamination of the nitrified water may thus lead to the more or less complete removal of the mineral nitrogen. The absence of nitrates may thus, under some circumstances, actually indicate contact with animal matter instead of freedom from it (Munro, Chem. Soc. Trans. 1886, 632).

It must also be remembered that, in the case of surface waters, the mineral nitrogen may undergo removal through being taken up as food by plant-life, and thus the evidence of previous contact with animal matters be destroyed.

As the hygienic significance of contact with animal matters consists in the possibility of the ingress of pathogenic microbes (which may at any time be present in sewage and similar animal refuse), it is obvious that the evidence of such previous contact afforded by the presence of mineral nitrogen in any excessive proportion must be viewed as serious, if the history of the water furnishes no guarantee that any such organised poisons which may have gained access would have been subsequently removed, whilst the evidence is of far less consequence, or may indeed become entirely negligible, if in the subsequent history of the water it has undergone processes of purification which practically preclude the possibility of such poisons being still present. Until the application of bacteriology to questions of water supply, it was not possible to ascertain the efficiency of processes of water purification in this respect. But we now know that the exhaustive filtration through porous strata which spring and deep well water has undergone practically guarantees the removal of any micro-organisms which may have been originally present; in the case of river and shallow well waters, on the other hand, the chance of such removal is much less, and hence in such waters the evidence afforded by mineral nitrogen of previous contact with animal matters must be viewed with suspicion, whilst in the spring and deep well waters it may often be disregarded altogether.

Chlorine. This element is invariably in a state of combination—generally as sodium chloride, and hence quite innocuous. Its determination in potable water, however, is of importance as often affording information as to whether the water has been in contact with refuse animal matters or not. In this respect it is often more useful than the mineral nitrogen, as, once present in water, it cannot by any natural processes be removed. Its diagnostic value is due to the fact that human urine contains 500 parts of chlorine, or 824 parts of common salt, in 100,000 parts. It is, of course, inapplicable in the vicinity of the sea and of natural salt deposits. In British waters free from animal pollution the average proportion of chlorine may be taken as 1 part per 100,000; but it is subject to very great variations.

There are, however, many other refuse liquids besides sewage which contain large quantities of chlorides, such as the effluents from dye and bleach-works, tanneries, paper-mills, alkali-works, and especially tin-plate and galvanising works, the proportion being often far in excess of anything ever found in sewage.

In America much attention has been bestowed on the proportion of chlorine present in unpolluted water at different distances from the sea-board. The points at which such waters exhibit the same amount of chlorine are joined by lines termed 'isochlors,' and these isochlors are found to be roughly parallel to the coast-line. Any water submitted for examination is then remanded for further inquiries if it exhibits more chlorine than is normal for the isochlor upon which the source of the particular water is situated. This is an attempt to make the chlorine a measure of the sewage contamination past and present, in much the same way as the proportion of total combined nitrogen has been employed by others. It has the advantage over the latter, inasmuch as the chlorine is practically permanent whilst the nitrogen is removable in various ways; but, on the other hand, the chlorine is subject to great variations within a small area, according to local circumstances, more especially geological. The chlorine, moreover, only testifies to contamination by liquid, and not by solid, excrements, and in this respect also is of less general applicability than the total combined nitrogen.

Hardness. This term is applied to those ingredients in water which react with soap and produce an insoluble 'curd,' the principal substances in question being the various salts of calcium and magnesium, which, entering into double decomposition with sodium stearate (hard soap) or potassium stearate (soft soap), give rise to calcium and magnesium stearates, both of which are insoluble bodies, and soluble salts of sodium or potassium. On this account the salts of calcium and magnesium are manifestly detrimental to the fitness of the water for washing. As regards the influence of these salts upon the quality of drinking water, opinion is divided. Some consider the presence of a certain proportion of these salts desirable as furnishing the materials necessary for bone-formation; others contend that if present in more than a moderate proportion they tend to cause calcareous concretions in the system, whilst, lastly, others regard their presence or absence as immaterial from a hygienic point of view. Further, by some authorities the sulphates and chlorides of calcium and magnesium (the so-called 'permanent hardness') are regarded as more objectionable than the bicarbonates or 'temporary hardness.' Again, there are many who view the presence of the salts of magnesium with more suspicion than those of calcium, and, indeed, magnesian waters are very generally credited with the power of causing phosphatic calculi, goitre, and cretinism. On this account it has sometimes happened that waters which were otherwise of most unimpeachable quality have been discarded in consequence of their containing a few parts per 100,000 of magnesia. All these views concerning the influence of calcium and magnesium salts are, however, based upon very unsatisfactory evidence. The Rivers Pollution Commissioners, in prosecuting their inquiry into this subject, found that 'where the chief sanitary conditions prevail with tolerable uniformity, the rate of mortality is practically uninfluenced by the softness or hardness of the water supplied to the different towns, and the average rate of mortality in the different water divisions varies far less than the actual mortality in the different towns of the same division. They were of opinion that, whilst waters of excessive hardness may be productive of calculus and perhaps other diseases, soft and hard water, if equally free from deleterious organic substances, are equally wholesome.' The question of magnesia in drinking water has been discussed by the writer ('What is the Importance of Magnesia in Drinking Water,' P. F. Frankland, Transactions of the Internat. Congress of Hygiene and

Demogr. London, 1891), from whose inquiry it appears that whilst the amount of magnesia in the water supplied to most large towns is very small—generally not more than 1–2 parts of MgO per 100,000—it is much larger than is generally supposed in the well-water consumed by such a large portion of the population. Thus in the case of fifty brewery waters from all parts of the kingdom, the average amount of magnesia (MgO) was 3·41 parts per 100,000. It must also be remembered that the geological formation richest in magnesia (the magnesian limestone) is only very slightly represented in this country, so that the proportions of magnesia met with in the dolomitic districts of the Continent must be much larger.

Until, therefore, a far more searching inquiry than hitherto has been made into the alleged effect of such waters upon health, it would appear undesirable that any importance should be attributed to such proportions of magnesia as the above in drinking waters which are otherwise of unimpeachable purity.

The effect of Clark's process on magnesian waters is noteworthy. As a general rule, the proportion of magnesia removed by the treatment with lime is small—much smaller than that of the lime removed; but it is particularly worthy of notice that in cases where caustic soda was used in conjunction with lime, as is now frequently done in the softening of water for industrial purposes, the magnesia may be removed in greater proportion than the lime, and as a matter of fact magnesium hydroxide is less soluble even than calcium carbonate.

The hardness of water not unfrequently throws light upon its previous history, for the food of both man and animals is of necessity rich in lime, and nearly the whole of this is in adult life again found in the liquid and solid excreta; hence water obtained from soil which has been much polluted with animal matters always exhibits a large amount of permanent hardness.

PURIFICATION OF DRINKING WATER.

Inasmuch as the impurities are either suspended or dissolved, mineral or organic, and the organic either animate or inanimate, it follows that the subject of purification may be considered from different points of view, according to the particular class of impurities the removal of which is under discussion. Until recently all the more important processes of drinking water purification were filtration processes, those depending upon precipitation being more especially of importance in connection with water for industrial purposes (*see* p. 706). Now, however, methods of more or less sterilising water by means of hypochlorites, ozone, or ultra-violet light are sometimes being resorted to (*see* p. 734).

Purification of drinking water on large scale. All surface water is liable to turbidity, and in times of rain and flood the amount of suspended matter may become excessive. It is, therefore, desirable that all surface water, even that from upland sources, should be submitted to purification before distribution for domestic purposes. The purification of surface water is best initiated by permitting the water to remain at rest in storage reservoirs for some days or even weeks, the greater part of the suspended matter thus becoming precipitated, and some destruction even of the dissolved organic matter also taking place. During storage most important biological changes also take place (*see* later). The process of filtration resorted to on the large scale is almost invariably that through sand of different degrees of coarseness. This method was inaugurated by Simpson, the engineer to the Chelsea Company in 1829, and has since been adopted in an ever-increasing number of places all over the world. The filter beds, as usually constructed, are 10–16 ft. in depth, often upwards of an acre in area, made water-tight with masonry, concrete, or puddled-clay walls. On the bottom are collecting drains, upon which is placed a layer of broken stone about 6 ins. in thickness, following upon which are layers of coarse gravel, fine gravel, and uppermost a stratum of fine sand, 1–4 ft. in thickness. The water is kept at a depth of 1–4 ft. above the surface of the fine sand, the rate of filtration varying in different works. For construction and cost of filtration plant, *see* Don and Chisholm, Modern Methods of Water Purification, London, 1911, 125. The greater part of the suspended impurities is retained in the downward passage of the water by the first few inches of fine sand, which sooner or later, sometimes in the course of a few weeks, causes the clogging of the filter. When the rate of filtration is too much retarded for practical purposes, the fouled surface of the sand is removed, after which the filtration can be continued until the filter is again choked, when the surface is again scraped off, the process being repeated until the stratum of sand becomes too thin to be efficient, after which the original thickness of the sand-layer is restored by means of washed sand. The sand scraped off is generally thoroughly washed, allowed to dry, and then used again. The particulars for the several sections of the Metropolitan supply, shown opposite, will serve to illustrate the method of working.

Besides the filter beds just described, some of the works drawing from the Thames are now using an auxiliary process of filtration through the natural gravel beds which form the banks of the Thames at Hampton. These gravel beds are at all times full of water, which forms, as it were, an underground river, and underground pipes are laid in this gravel and connected with a pumping well in order to utilise this water, which is always clear and bright in consequence of the natural filtration which it has undergone. In order to increase the supply of this underground water the gravel bed is flooded with water directly from the Thames, for which purpose a second series of perforated pipes are laid parallel to the first and placed at a distance of about 30 yards from them. This second series of pipes is placed in direct communication with the Thames, but at the point of ingress is placed a small vertical sand filter to arrest the coarser impurities.

Such sand filters, although very efficient in removing the suspended matter, have comparatively little action upon that which is dissolved. Thus the following figures exhibit the composition of the York water supply, before and after filtration through sand :—

(Results of analysis expressed in parts per 100,000.)

	Before filtration	After filtration
Total solid matters	28·40	26·20
Organic carbon	0·123	0·119
Organic nitrogen	0·025	0·022
Ammonia	0	0
Nitrogen as nitrates and nitrites	0·077	0·089
Chlorine	1·6	1·6
Temporary hardness	11·5	10·9
Permanent hardness	7·1	7·1
Total hardness	18·6	18·0
Micro-organisms (colonies yielded by 1 c.c. of water on cultivation with gelatin-peptone)	31,200	122

It was formerly supposed that such sand filtration could have little or no effect in removing the micro-organisms present in water, as the interstitial spaces between the grains of sand are so large in comparison with the minute dimensions of the microbes. It was first shown by Koch in Germany, and by the writer in this country, that nearly all the microbes in water may be removed by the sand-filters (Koch, Bericht der Deputat. f. die Verwaltung der Canalisationswerke, Berlin, 1883; P. F. Frankland, Proc. Roy. Soc. 1885; Proc. Inst. Civ. Engineers, 1885–6; J. Soc. Chem. Ind. 1885, 1887), and this result has been since confirmed by many other investigators.

It was, in fact, supposed by Koch and his pupils that the sand filtration really removed *all* the microbes originally present in the water, and that those always found in the filtered water had gained access subsequent to filtration. The writer had, however, from the first shown that in the case of his regular examinations of the London water supply there was an obvious relationship between the number of microbes in the unfiltered and filtered waters respectively, necessitating the conclusion, therefore, that the sand filters can only be credited with removing *a portion and not the whole of the micro-organisms present.* This is sufficiently conspicuous from the tables on next page, which record some of the writer's results obtained with the London water supply during the year 1886, and reported to the Local Government Board (P. F. Frankland, J. Soc. Chem. Ind. 1886). The unfiltered Thames water was in every case collected near the intakes of the several water companies at Hampton, and the filtered water from the mains of the Chelsea, West Middlesex, Southwark, Grand Junction, and Lambeth Companies respectively.

METROPOLITAN WATER SUPPLY, JANUARY, 1911.

District works	Number of days' storage	Filtering area per million gallons of the average daily supply of 1910	Thickness of sand on filters		Average rate of filtration per square foot per hour
			Maximum	Minimum	
		acres	ft. ins.	ft. ins.	gallons
Eastern	52·5	0·676	2 6	1 6	1·37
New River	10·7	0·590	2 3	1 7	1·84 2·13 Kempton Park
Southern, Lambeth Works	35·7	0·986	3 0	2 6	1·05
„ Southwark „			3 0	2 3	1·17
Western, Chelsea Works	11·5	1·007	4 3	3 3	1·43
„ Grand Junction Works			3 0	2 3	0·82 Hampton 0·70 Kew Bridge
„ West Middlesex Works			2 9	2 6	1·17

Monthly Reports by Metropolitan Water Examiner to Local Government Board.

C. Fraenkel and Piefke (Zeitsch. Hygiene, 8, 1890, 1–40) subsequently demonstrated by direct experiment that particular species of bacteria purposely introduced into the unfiltered, were still present, although in greatly-diminished numbers, in the filtered water.

The wonderful efficiency of these sand filters in removing microbes was at first very difficult to account for, but it is now recognised to depend upon the impervious nature of the slimy deposit which forms upon the surface of the sand, and until such a coating has been established the filter has but little effect in removing micro-organisms (Piefke, Aphorismen über Wasserversorgung, Zeitsch. Hygiene, 7, 1889, 115–170). This slimy deposit consists not only of silt, mud, and colloidal matter, but also of a multitude of living forms—diatoms, green and blue algæ, innumerable bacteria, fungi, and protozoa. Many of these forms actually feed on bacteria. The rate at which filtration is carried on is also a most important factor, the more rapid the rate the less efficient being the purification (P. F. Frankland, Proc. Inst. Civ. Engineers, 1885–6). Although the removal of bacteria is not attributable to the sand particles as such, there is abundant evidence that the finer the sand and the greater its depth the more efficient is the filtration. This is doubtless due to a better support being given to the filtering skin, and to the finer and thicker layer of sand regulating the passage of water through the medium, whilst the water is also brought into more intimate and prolonged contact with the colloidal matter with which the sand of a matured filter is clothed. The statistics of the London waterworks show that the cost of filtration as carried out by them averages about 0·6*d.* per 1000 gallons.

Table I. 1886.

Total number of Colonies obtained by cultivation of one cubic centimetre of water.

—	Description of water					
	Thames unfiltered	Chelsea	West Middlesex	Southwark	Grand Junction	Lambeth
January	45,400	159	180	2270	4894	2587
February	15,800	305	80	284	208	265
March	11,415	299	175	1562	379	287
April	12,250	94	47	77	115	209
May	4,800	59	19	29	51	136
June	8,300	60	145	94	17	129
July	3,000	59	45	380	14	155
August	6,100	303	25	60	12	1415
September	8,400	87	27	49	17	59
October	8,600	34	22	61	77	45
November	56,000	65	47	321	80	108
December	63,000	222	2000	1100	1700	305
Average	20,255	146	234	524	630	475

Table II. 1886.

Percentage reduction in the number of developable micro-organisms present in the river waters before delivery by the companies.

—	Description of water				
	Chelsea	West Middlesex	Southwark	Grand Junction	Lambeth
January	99·7	99·6	95·0	89·2	94·3
February	98·1	99·5	98·2	98·7	98·3
March	97·4	98·5	86·3	96·7	97·5
April	99·2	99·6	99·4	99·1	98·3
May	98·8	99·6	99·4	98·9	97·2
June	99·3	98·3	98·9	99·8	98·5
July	98·0	98·5	87·3	99·5	94·8
August	95·0	99·6	99·0	99·8	76·8
September	99·0	99·7	99·4	99·8	99·3
October	99·6	99·7	99·3	99·1	99·5
November	99·9	99·9	99·4	99·9	99·8
December	99·7	96·8	98·3	97·3	99·5
Average percentage reduction	98·6	99·1	96·7	98·2	96·2

In countries liable to extreme cold—indeed, even in cold winters in this country—the process of sand filtration offers great difficulties, in consequence of the freezing of the filters; and this has, in Berlin, been guarded against by the construction of a number of covered filter-beds. In the United States, where the same difficulty exists, the Hyatt system of filtration has been employed on a considerable scale. In this the water is first treated with a minute quantity of alum (about ¼ grain per gallon), after which it passes through a steel filtering chamber, consisting of a vertical cylinder the diameter of which is nearly twice its height. This cylinder is divided by a horizontal diaphragm, capable of withstanding the hydrostatic pressure necessary for rapid filtration. The lower half contains the filtering material, composed of 2 parts coke and 3 parts sand. The upper part of the cylinder is used for washing the filtering material, which at regular intervals is transferred into it in a state of violent agitation by hydraulic currents, the impurities flowing away through pipes situated near the top of the cylinder. In the process of filtration the water is admitted through pipes to the upper part of the lower section of the cylinder, and it is drawn off through perforated cups, which permit the water, but not the sand, to pass. It is claimed that the efficiency of the system depends more upon the successful precipitation and entanglement of germ life by the coagulant alumina than upon any special merits of the filter (Potable Water, Floyd Davis, Iowa, U.S. 1891). The cost of maintenance is said to be only one-fifth of that entailed by filter beds.

In recent years the use of mechanical filters has been gaining ground in Great Britain also, the Jewell, Bell, and Candy filters being those most commonly employed (*see* Modern Methods of Water Purification, Don and Chisholm, London, 1911; *see* also *Bacteriology of water*, below). The Puech-Chabal system consists in submitting the water to successive processes of filtration, sometimes as many as six stages, beginning with coarser grades of gravel and ending with fine sand, being employed. It is specially suitable for very turbid waters, as the life of the fine sand filter is greatly prolonged.

It has been used at Magdeburg and other places (*see* Don and Chisholm, *l.c.*).

Of other methods of drinking-water purification on the large scale the only one that need be mentioned is Anderson's. The method consists in passing the water slowly through revolving iron cylinders about two-thirds filled with iron borings. A small quantity of the iron continuously passes into solution, so that the water becomes impregnated with ferrous iron, which subsequently, when the water flows into a settling tank, is converted into the ferric state with precipitation, a large proportion of the organic matter in solution being removed in the process, whilst a very considerable diminution in the number of vital germs is also effected. After undergoing oxidation in the settling tank, the water is finally filtered through sand before distribution. It takes 3½ mins. for the water to pass through the rotating cylinder, the entire process occupying about 6 hours (Anderson, Proc. Inst. Civ. Engineers; Engineering, 39, 525). This process has been used on a large scale at Antwerp and Paris.

Purification of drinking water on the small scale. The filtration of water on the small scale was already known to the ancients. Thus Pliny mentions vessels in which water was clarified by passage through wool. An immense number of different materials have been employed during recent years, but space will only permit of the brief consideration of a few of the more important ones.

Animal charcoal is employed in a number of common household filters, and from the invaluable services which it yields in sugar-refining it was anticipated that it would be highly efficient as a water filter. Unlike sand, it not only acts upon the suspended matters, but also removes a considerable proportion of the dissolved organic matter, and even some of the temporary hardness. Unfortunately, however, its action is very transient, and it generally soon becomes the seat of numerous organic growths, which are favoured by the calcium phosphate it contains, and the filtered water is then often rendered more impure than the unfiltered.

Vegetable charcoal has but little effect on the dissolved organic matters, although if in a sufficiently fine state of division it is an excellent strainer for suspended impurities (*see* table below).

Bischof's spongy iron, obtained either by reduction of hæmatite or of roasted pyrites, has a remarkable power of removing dissolved organic matters, as well as temporary hardness and nitrates, and this power is far more permanent than that of animal charcoal. It was for some time also employed on the large scale, in conjunction with sand, at the Antwerp Waterworks. The effect of filtration through animal charcoal and spongy iron respectively is exhibited in the table below.

Since the recent great advances in bacteriological science, it has become evident that the removal of micro-organisms from drinking water is a matter of much greater importance than the removal of organic matter, and hence it is in respect of this property that the value of filters is now generally estimated. The writer has shown (The Removal of Micro-Organisms from Water, P. F. Frankland, Proc. Roy. Soc. 1885) that several substances—such as coke, wood-charcoal, spongy iron, &c.—in a sufficiently fine state of division are capable of entirely removing all microbes in water passed through a stratum of a few inches of these materials. This power, which is quite independent of any chemical action (thus in the case of coke and wood-charcoal there is little or no removal of dissolved organic matter), is, however, not maintained unless the materials are frequently renewed; and in the case of animal charcoal which has been in use for a short time (one month) the number of microbes was found to be far greater in the filtered than in the unfiltered water. The most conspicuous instance of biological, as opposed to chemical, filtration is furnished by Chamberland's unglazed porcelain filter, which entirely removes microbes, but has no chemical action whatever (*see* table below).

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness			No. of developable micro-organisms in 1 c.c. of water
								Temporary	Permanent	Total	
London water, unfiltered [1]	24·60	0·129	0·023	0	0·188	0·211	1·6	—	—	19·4	—
Ditto, after filtration through fresh animal charcoal [1]	19·40	0·029	0·007	0·013	0·194	0·212	1·6	—	—	15·2	—
London water, unfiltered [1]	25·94	0·164	0·030	0·002	0·062	0·094	1·9	—	—	19·7	—
Ditto, after filtration through animal charcoal in use 11 months [1]	25·10	0·010	0·002	0·002	0·125	0·129	1·9	—	—	19·1	—
London water, unfiltered [1]	25·28	0·120	0·013	0	0·166	0·179	1·7	14·5	6·7	21·2	—
Ditto, after filtration through fresh spongy iron [1]	13·70	0·025	0·004	0·002	0·031	0·037	1·7	7·4	4·6	12·0	—
London water, unfiltered [1]	24·10	0·188	0·034	0·001	0·120	0·155	1·95	11·8	7·3	19·1	—
Ditto, after filtration through spongy iron in use 8 months [1]	14·84	0·089	0·020	0·001	0	0·021	1·95	5·3	4·3	9·6	—
Water, before filtration [2]	24·80	0·144	0·050	0	0·190	0·240	1·9	11·3	5·6	16·9	26,000
Ditto, after filtration through fine coke [2]	25·00	0·107	0·038	0	0·202	0·240	1·9	11·3	5·6	16·9	0
Ditto, after filtration through fine wood charcoal [2]	24·68	0·090	0·024	0	0·221	0·245	1·9	12·5	4·6	17·1	0
London water, before filtration [3]	33·70	0·282	0·028	0	0·288	0·316	1·9	15·7	4·9	20·6	54
Ditto, after filtration through Chamberland filter [3]	30·04	0·284	0·027	0	0·289	0·316	1·9	14·4	5·3	19·7	0

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[1] Riv. Commis. 6th Rep.

[2] P. F. Frankland, J. Soc. Chem. Ind. 1885.

[3] P. F. Frankland, Proc. Roy. Soc., 1885, 390.

A number of household filters in actual use have been examined with regard to their power of removing microbes by Plagge (Public Health Section of Germ. Assoc. of Naturalists and Physicians, 1886), who divides them into six classes, according to the materials used: (1) *carbon filters*, (2) *stone and sand filters*, (3) *spongy-iron filters*, (4) *paper filters*, of several kinds, (5) *porous earthenware filters* (Chamberland), (6) *asbestos filters* (Breyer, Hesse, Arnold, and Schirmer). The carbon filters were found not only to admit of the free transmission of microbes, but in some cases the numbers in the filtrate greatly exceeded those in the unfiltered water. Thus in one case 68 colonies were obtained from 1 c.c. of the unfiltered, and 12,000 from 1 c.c. of the filtered, water. The stone and sand filters were all found to be worthless. The spongy-iron filter yielded the following results: unfiltered water, 38,000 colonies from 1 c.c.; filtered, 18,000–24,000 colonies from 1 c.c. The paper filters all yielded very unsatisfactory results; the earthenware and asbestos filters, on the other hand, gave in nearly every instance a filtrate practically free from microbes. (For particulars concerning the sterilising power of the Chamberland filter, *see* also Miquel, Analyse Bactériologique des Eaux, Paris, 1891.) The principal drawback to these porous earthenware filters is the rapid diminution in the rate of filtration which they exhibit. More satisfactory in this respect are the Berkefeld filters, similarly constructed of burnt infusorial earth (Nordtmeyer, Zeitsch. Hygiene, 1891, 10, 145; Bitter, *ibid.* 155). Neither the Chamberland nor Berkefeld filters permanently yield sterile water, some of the bacteria in the unfiltered water sooner or later growing through the pores. It is, however, doubtful whether any of the ordinary pathogenic bacteria would do this, as none of them are known to actually multiply extensively in ordinary drinking water (Kübler, Zeitsch. Hygiene, 1890, 10, 48).

Purification of drinking water by distillation. This is, of course, the most effectual mode of freeing water from all its impurities. It is resorted to, on a considerable scale, at sea, both for steam and sailing vessels. (For description of forms of apparatus in actual use *v.* Fischer, Technologie d. Wassers, Brunswick, 1880, 201–208.) The insipid taste of the distilled water can be removed either by aëration, or by filtration through animal charcoal or other porous substances. Distilled water is also employed to some extent for the manufacture of aërated waters and for artificial ice.

Purification of drinking water by boiling. The purification consists, of course, only in the destruction of living organisms present in the water, but this is from an hygienic point of view of the greatest importance. In its action it is far more reliable than any process of filtration, and should be invariably resorted to in the case of waters which bear any suspicion of sewage contamination. The vapid taste of the boiled water may be removed by passage through a filter, which, however, should be exclusively employed for this purpose and not for filtering unboiled water. A convenient form of apparatus for sterilising large quantities of water—*e.g.* for hospitals, barracks, &c.—is described by Miquel (Manuel d'Analyse bactériologique des Eaux, Paris, 1891, 188). The more extensive use of boiled instead of filtered water is one of the chief sanitary desiderata of the day. Although absolute sterility cannot be *guaranteed* by a few minutes' ebullition, yet the reduction in the number of microbes by this simple process is so great that it may be safely regarded as ample for practical purposes. Thus Miquel and Wada (*ibid.* 185) found in the case of the Ourcq canal water of Paris:—

Temperature	Bacteria in 1 c.c.
14°C.	460,800
50° for 10 minutes . .	600
60° ,, . .	(60)
70° ,, . .	88·8
80° ,, . .	62·4
90° ,, . .	26·4
100° ,, . .	0·5
100° for 20 minutes . .	0·0

WATER FOR INDUSTRIAL PURPOSES.

Of the numerous industrial uses to which water is put, the most general and important is the raising of steam. The composition of the water supplied to steam-boilers is a matter of great consequence, as the use of unsuitable water may cause the corrosion of boiler-plates and the formation of deposits, which not only occasion a serious loss of heat but may also lead to most disastrous explosions (*v.* BOILER INCRUSTATIONS AND DEPOSITS).

Water for other industrial purposes. (1) For *brewing*, *see* art. BREWING. For use in bakeries, the water should be in all respects of the same degree of purity as is demanded for drinking purposes.

(2) For the *textile industries* the character of the water employed is often of great consequence. Thus in bleaching and dyeing the presence of iron and manganese, even in very small quantities, is highly deleterious, giving rise to iron and manganese stains on the bleached goods, and causing spots and modifications in the shades of dyed materials. Hard water, again, involves the use of larger quantities of alkali and soap in the several operations of boaking, scouring, and milling, and the insoluble lime-soap is left adhering to the fibre, often preventing the subsequent application of mordant or dye. In those operations, again, in which dyed fabrics are soaped, the lime-soap often injures the brilliancy of the colour, whilst in other cases the earthy soaps precipitated on the fibre act as mordants, and attract the colouring matters on those parts of the goods where it is not wished to fix them. In general, hard water has the effect of dulling many colours, and if due to bicarbonates retards, or even prevents, the dyeing of such colours as require an acid bath (*e.g.* cochineal scarlet). In some cases hard water containing bicarbonates wastes the mordants by precipitation in the bath instead of on the fibre, whilst it is sometimes actually beneficial for the washing of goods which have been mordanted with basic mordants. Such water is unsuitable for the solution of many coal-tar colours—*e.g.* methyl violet—a portion of the latter being lost as a tarry precipitate, whilst the goods are often spotted. For dyeing with some colours—*e.g.* alizarin and logwood—the presence of a certain amount of lime is almost indispensable; a pure water to which a know

quantity of lime-salt has been added is, however, preferable to a naturally hard water, especially if the latter is of variable composition. Water containing alkaline carbonates is sometimes advantageous, *e.g.* in wool-scouring, and in those dyeing operations in which the addition of sodium carbonate is prescribed; but in mordanting, in the dyeing with many colours, and in the washing of dyed goods, it is often very prejudicial; in these cases it should be neutralised with sulphuric or acetic acid. Acid waters are generally highly injurious, and should be neutralised with sodium carbonate. Sulphuretted hydrogen in water is also very objectionable in many operations of dyeing, more especially in mordanting with metallic salts (Hummel, Dyeing of Textile Fabrics). For the manufacture of *paper*, water containing iron is highly objectionable, giving rise to stains, whilst the presence of hardness is objectionable in causing the decomposition of the rosin-soap.

(3) For *tanning*, pure water is also a desideratum. Water much contaminated with organic matter causes injury to the surface of the leather, and sometimes a corrosion from the flesh-side of the skin. Water containing carbonic acid, or the bicarbonates, or calcium and magnesium sulphates, causes the hides to swell, whilst the chlorides prevent the swelling, and hence sea-water cannot be employed for the purpose. Hard water occasions a less perfect utilisation of the tanning materials, and an excess of chlorides retards the tanning process and causes the leather to attract moisture; the presence of iron is not so objectionable as is commonly supposed (Fischer, Das Wasser, 49–51).

(4) In *sugar-refining* the sulphates and alkaline carbonates are more productive of molasses than the chlorides, whilst nitrates are specially objectionable, as they prevent the crystallisation of six times their weight of sugar (Fischer, Technologie d. Wassers, p. 286).

Purification of water for industrial purposes.

As already pointed out, some substances, although unobjectionable in drinking water, operate prejudicially when the water is employed for many industrial purposes, and numerous methods have been devised for removing these impurities or for counteracting their effects. But few methods of purification have found favour in actual practice, and to these alone will any attention be given here. The processes which have for their object the removal of matters in suspension and organic substances have been already described under *Purification of drinking water* (*v.* p. 702), whilst the processes intended for the improvement of industrial water supplies are chiefly directed to the removal of lime and magnesia salts in solution, which, as has been shown above, interfere with the success of so many industrial operations. This removal of lime and magnesia salts is frequently spoken of as 'water-softening,' in consequence of the water after such treatment requiring less soap when used for washing purposes.

Purification with lime (Clark's process). This method of purification was first proposed by Clark, of Aberdeen, in 1841, and consists in the decomposition of calcium bicarbonate or 'temporary hardness' of water by the addition of a suitable quantity of slaked lime, according to the equation

$$\underset{\text{Calcium bicarbonate}}{CaH_2(CO_3)_2}+Ca(OH)_2=\underset{\text{Calcium carbonate}}{2CaCO_3}+2H_2O.$$

Thus both the lime in solution as bicarbonate as well as that added in the form of hydroxide are precipitated as normal carbonate, which is almost insoluble in water. The calcium hydroxide is sometimes added in the form of milk of lime, sometimes in that of clear lime-water, but the latter is far preferable, as the quantity added can be more easily controlled and an excess avoided. The necessary quantity of calcium hydroxide is most easily ascertained by adding such an amount that, after thorough mixing, a small quantity of the water taken out yields a yellow or brown colour with a solution of silver nitrate, more water is then added, until, on similarly testing, no coloration with the silver nitrate is obtained. This test should invariably be resorted to even in the case of such waters as are of very constant composition, and which, therefore, admit of the lime being proportioned by experience, as otherwise an excess or deficiency of lime is nearly sure to result. In its original form the Clark process is carried out in large tanks in which the water can remain at perfect rest for about 16 hours, although by the use of a floating exit-pipe the clear surface water can often be drawn off after 2 or 3 hours, and before the whole of the precipitate has reached the bottom. This method has been most successfully employed on a large scale at the Colne Valley Waterworks, near Bushey, at Canterbury, Caterham, and many other places on a small scale. The 'temporary hardness' only is, of course, removed, and even this not completely, as under the most favourable circumstances a small proportion of calcium carbonate remains in solution, whilst in the case of waters containing magnesium bicarbonate the removal of the latter is generally far less complete. In addition to these bicarbonates, the salts of iron and much organic matter are also removed.

In order to obviate the large amount of storage capacity required for Clark's process, several modifications have been introduced, in which the precipitate formed by the treatment with lime is either removed by filtration or made to rapidly subside by artificial means. The most notable of these improved processes are the so-called 'Porter-Clark,' in which the precipitate is removed with a filter-press, and Gaillet and Huet's process, in which subsidence is promoted by causing the water to take a circuitous zig-zag and upward path after the addition of the lime. In this latter process both lime and caustic soda are frequently employed in conjunction as the softening agents; in this manner both 'temporary' and 'permanent' hardness can be, to a great extent, removed, thus:—

$$CaH_2(CO_3)_2+2NaOH=CaCO_3+Na_2CO_3+2H_2O$$
$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

Space does not permit the description of a number of other water-softening apparatuses which are now on the market, and which only differ from each other in the special mechanical devices for supplying the chemicals (milk of lime, lime water, sodium carbonate, or caustic soda, as the case may be) and for removing the deposit. The Archbutt-Deeley process, however, possesses certain features of interest. In this the clarification of the treated water is accelerated by stirring it up with the sludge of calcium carbonate obtained in previous precipitations, this being effected by blowing in compressed air through perforated pipes. The subsequent sedimentation takes place very rapidly, and the clear water is drawn off from the surface by means of a floating arm. Further, the danger of subsequent deposition of calcium carbonate in the service pipes, which often occurs when an insufficient time is allowed for sedimentation, is avoided by injecting carbon dioxide (obtained from a coke-stove, the gas being scrubbed with limestone to remove sulphur compounds) into the clarified water as it is drawn from the settling tank.

Magnesia has also been employed to a limited extent for softening instead of lime. Under these circumstances the following reactions may take place, especially if heat is applied :—

$$CaH_2(CO_3)_2+MgO=CaCO_3+MgCO_3+H_2O$$
$$MgCO_3+CaSO_4=CaCO_3+MgSO_4$$
$$MgCO_3+CaCl_2=CaCO_3+MgCl_2$$

(Fischer, Chem. Technol. d. Wassers, Brunswick, 1880, 264).

The formation of magnesium chloride is obviously disadvantageous for boiler purposes.

A number of other processes of chemical purification have from time to time been suggested, but none of them has met with any great success. Thus attempts have been made to utilise the following reactions :

$$CaH_2(CO_3)_2+Ba(OH)_2=CaCO_3+BaCO_3+2H_2O$$
$$CaSO_4+Ba(OH)_2=BaSO_4+Ca(OH)_2$$
$$CaSO_4+BaCl_2=BaSO_4+CaCl_2$$
$$CaH_2(CO_3)_2+\underset{\substack{\text{Sodium}\\ \text{oxalate}}}{C_2O_4Na_2}=\underset{\substack{\text{Calcium}\\ \text{oxalate}}}{C_2O_4Ca}+\underset{\substack{\text{Sodium}\\ \text{bicarbonate}}}{2NaHCO_3}$$
$$CaSO_4+C_2O_4Na_2=C_2O_4Ca+Na_2SO_4$$
$$CaCl_2+C_2O_4Na_2=C_2O_4Ca+2NaCl$$
$$CaH_2(CO_3)_2+2HCl=CaCl_2+2CO_2+2H_2O$$

In the *Permutite* process, devised by Dr. Gans of Berlin, the water is softened by filtration through artificial zeolite (a hydrated silicate of alumina and soda) to which the name of *Permutite* has been given. The latter is made by fusing together silica or quartz, alumina or china-clay, and sodium carbonate. The fused mass is extracted with water, a crystalline body ($SiO_2=46$, $Al_2O_3=22$, $Na_2O=13{\cdot}6$, $H_2O=18{\cdot}4$ p.c.) being obtained. When waters containing calcium or magnesium salts are filtered through this material, the following reactions take place :—

$$Na_2Al_2Si_2O_8+CaCO_3=Na_2CO_3+CaAl_2Si_2O_8$$
$$Na_2Al_2Si_2O_8+CaSO_4=Na_2SO_4+CaAl_2Si_2O_8$$

It is claimed for this process that the whole of the hardness is removed and that the calcium or magnesium zeolite formed can be reconverted into the original permutite or sodium zeolite by treatment with a strong solution of common salt.

Gans uses a manganese-permutite (silica, alumina, and a higher oxide of manganese) for the removal of iron and manganese in water. This material can be regenerated by treatment with a solution of potassium or calcium permanganate. The manganese-permutite can also be employed for the sterilisation of wat the water is treated with permanganate sufficient concentration to destroy bacteria, and on subsequent filtration through mangane permutite, the whole of the manganese is sa to be retained by the filter. Calcium-permuti has been used for removing potash from molass lime passing into solution; the lime may replaced by soda by passing through sodium permutite.

For the effect of softening processes on th bacteria in water, *v.* p. 732.

The action of water on lead, zinc, copper, an aluminium. The action of water on thes metals, and especially on lead, is of grea importance in connection with the distribution and storage of water. The Roman employed leaden pipes, and Vitruvius and Gale were aware that some waters were thereby rendered deleterious. On the other hand certain waters have so little action on lead tha pipes of this material have been in use for upwards of 200 years without showing any trac of corrosion (Fischer, Technologie d. Wassers 317). As a general rule, hard waters, and mor especially those containing bicarbonates, do n act on lead; the greater number of activ waters are soft, and generally entirely destitut of bicarbonates. The activity has been ascribe by different authorities to the presence absence of a great variety of ingredients in th water—*e.g.* the presence of dissolved air (Yorke ammonium nitrite (Medlock), ammonium carbonate (Böttcher). Some have contended tha organic matters diminish the activity (Horsford others that they increase it (Hofmann, Graham Miller, and Noad). The latter authorities wer of opinion also that the presence of dissolve oxygen and the absence of more than 3 vol of carbon dioxide in 100 vols. of water ar amongst the conditions necessary for the attac upon lead. It has also been contended that minute proportion of calcium phosphate prevent a soft water from attacking lead (Riv. Pollu Commiss. 6th Rep. 224), whilst according others, again, the protecting ingredient is sili (Crookes, Odling, and Tidy, Report on the Acti of Water on Lead, London, 1886). In man cases the activity of the water is due to th presence of organic acids (Allen), this bein doubtless a fruitful cause of moorland wate acting on lead. The activity of many waters confined to new untarnished lead, whilst othe continue to act, sometimes with increas vigour, on the old and tarnished metal (P. Frankland, The Action of Water on Lead. Soc. Chem. Ind. 1889, 241).

Numerous expedients have been resorted in order to destroy this activity of some waters. When acidity is the presumable ca the most obvious remedy is the filtration of water through finely-divided limestone; in prac tice, however, this is found to be only of tem porary service, as the surfaces of the limest become coated with a film which prevents th being further acted on by the water. It has be found more effective to continuously mix water with a milk of finely-divided calc carbonate, and allowing this to subside be the water is distributed.

It is now generally admitted that the ac of water on lead is of two different kinds.

these the most obvious is that due to the acidity[1] of some waters, such acidity may be due to organic or even mineral acids, and can be determined by titration with appropriate indicators. Such acid waters have, in general, a continuous action on lead. The acidity can, of course, be neutralised by the addition of lime, finely-divided calcium carbonate, or most effectively by sodium carbonate. It was, however, shown many years ago by the writer that such neutralisation does not necessarily entirely stop the action of the water on lead, and that this is often only secured by adding a considerable excess of sodium carbonate. Similarly there are many natural waters, which, although slightly alkaline with small proportions of calcium bicarbonate, nevertheless act on lead. Such action of neutral or even slightly alkaline waters is now usually termed '*erosive*' as distinguished from the '*plumbosolvent*' action of acid waters. These remarkable phenomena have only received a satisfactory explanation since the recent advances in physical chemistry have illuminated the subject of chemical equilibrium.

This matter is very ably dealt with in an important paper by Paul, Ohlmüller, Heise, and Auerbach (Arbeiten a. d. kais. Gesundheitsamte, 1906, 23; Untersuchung über die Beschaffenheit des zur Versorgung der Haupt- und Residenzstadt Dessau benutzten Wassers, insbesondere über dessen Bleilösungsfähigkeit). The conclusions arrived at by these authors are :—

1. *Dissolved oxygen* is necessary for the solution of metallic lead in pure water. Experiments made with distilled water, which had been saturated with air freed from carbon dioxide, showed that nearly the whole of the oxygen (amounting to about 9 mgms. per 1 litre) was taken up presumably according to the equation :

$$2Pb+2H_2O+O_2=2Pb(OH)_2.$$

The water, which was at 18°, took up about 115 mgms. of lead per 1 litre. By increasing the proportion of oxygen in the air used for saturating the water the amount of lead taken up was at first also increased (up to about 140 mgms. Pb per 1 litre), but this was followed by a sudden drop to an amount which remained practically constant (about 108 mgms. per 1 litre for about 14·5 mgms. O_2 dissolved in 1 litre water). This sudden drop is referred to the appearance of a precipitate (*solid phase*) preventing further supersaturation of the water with lead hydroxide. (The authors did not determine the exact composition of the solid phase, which may have been $Pb(OH)_2$, or more probably one of its anhydrides.)

2. *Free carbonic acid* diminishes the plumbosolvent effect of the simultaneously present dissolved oxygen. Thus, in an experiment with distilled water made to contain about 8 mgms. O_2 and 40 mgms. CO_2 in 1 litre, the amount of lead taken up was about 11 mgms. per 1 litre, or about $\frac{1}{10}$ of that dissolved when the same proportion of dissolved oxygen was present in the absence of carbonic acid. This diminished plumbosolvency is, of course, attributable to the formation of a more insoluble solid phase, viz. either $PbCO_3$, or more probably some basic carbonate such as $2PbCO_3,Pb(OH)_2$.

3. *Sodium bicarbonate* in the absence of any appreciable quantity of free carbonic acid greatly reduces the plumbosolvency of water, thus in similar experiments, in which the same proportion (about 9 mgms. O_2 per 1 litre) of dissolved oxygen was retained, but along with 35 mgms. of $NaHCO_3$ per litre, the amount of lead taken up was only 0·6 mgms. per litre of water. This, again, is attributable to the diminished solubility of the solid phase in the solution of the sodium bicarbonate. The amount of lead taken up by the water is limited by the *solubility product;* thus a saturated solution of lead carbonate will contain a small concentration of $PbCO_3$ molecules, together with $Pb^{\cdot\cdot}+CO_3''$ ions, of which only the $PbCO_3$-molecules are in direct equilibrium with the solid phase (precipitated lead carbonate). The concentration of the $PbCO_3$ molecules will always remain constant as long as there is any of the solid phase present, but this concentration is very small. The concentration of the ions, on the other hand, is determined by the dissociation equilibrium. Thus, representing the molecular concentrations of the respective bodies by the formulæ enclosed in brackets, we have—

$$[Pb^{\cdot\cdot}]\times[CO_3'']=k\times[PbCO_3],$$

in which k is a constant. But in saturated solutions, as already seen above, $[PbCO_3]$ is constant, therefore $k\times[PbCO_3]$ is also constant, and can be represented by S, which is termed the *solubility product*, thus—

$$[Pb^{\cdot\cdot}]\times[CO_3'']=S$$

$$\therefore\ [Pb^{\cdot\cdot}]=\frac{S}{[CO_3'']}$$

which obviously signifies that the concentration of the $Pb^{\cdot\cdot}$-ions will be the smaller the greater the concentration of the CO_3''-ions. (If the solid phase is a basic carbonate, then it can be shown that the concentration of the $Pb^{\cdot\cdot}$-ions must be inversely proportional to the concentrations of the CO_3''- and the OH'-ions.)

In solutions of free carbonic acid the concentration of CO_3''-ions is very small (because carbonic acid being a very weak acid is only very slightly dissociated into ions), whilst in solutions of $NaHCO_3$ the concentration of CO_3''-ions is much greater, and, therefore, the concentration of the $Pb^{\cdot\cdot}$-ions will be correspondingly diminished, or, in other words, a much smaller proportion of lead will pass into solution. (It should be mentioned that the phenomena may be complicated by the circumstance that the nature of the solid phase may be different according as the metallic lead is placed in contact with a solution of free carbonic acid or bicarbonate respectively.)

4. The simultaneous presence of *free carbonic acid and sodium bicarbonate* leads to the following considerations :—

$$CO_2+H_2O \rightleftarrows H_2CO_3$$

further $H_2CO_3 \rightleftarrows H^{\cdot}+HCO_3'$, whilst to a much less degree $HCO_3' \rightleftarrows H^{\cdot}+CO_3''$. These dissociations are regulated by the equations

$$(1)\ [H^{\cdot}]\times[HCO_3']=k_1\times[H_2CO_3]$$

$$(2)\ [H^{\cdot}]\times[CO_3'']=k_2\times[HCO_3'].$$

in which the values

$$k_1=3{\cdot}04\times10^{-7}$$

$$k_2=1{\cdot}3\times10^{-11}$$

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[1] See a very important paper on 'The Acidity and Alkalinity of Natural Waters,' by James Walker and S. A. Kay (J. Soc. Chem. Ind. 1912, 31, 1013).

are known (J. Walker and W. Cormack, Chem. Soc. Trans. 1900, 77, 5; Bodländer, Zeitsch. physikal. Chem. 1900, 35, 23).

From equation (2)

$$[\mathrm{CO}_3''] = k_2 \times \frac{[\mathrm{HCO}_3']}{[\mathrm{H}^{\cdot}]}$$

and combining this with equation (1) we have

$$[\mathrm{CO}_3''] = \frac{k_2}{k_1} \times \frac{[\mathrm{HCO}_3']^2}{[\mathrm{H}_2\mathrm{CO}_3]}$$

but with PbCO_3 as solid phase we had

$$[\mathrm{Pb}^{\cdot\cdot}] = \frac{\mathrm{S}}{[\mathrm{CO}_3'']}$$

which can, therefore, be written

$$\mathrm{Pb}^{\cdot\cdot} = \frac{\mathrm{S} \times k_1}{k_2} \times \frac{[\mathrm{H}_2\mathrm{CO}_3]}{[\mathrm{HCO}_3']^2}$$

But, inasmuch as free carbonic acid is very little, and sodium bicarbonate very much dissociated, the value of $[\mathrm{H}_2\mathrm{CO}_3]$ may be taken as proportional to the molecular concentration of the free carbonic acid, and $[\mathrm{HCO}_3']$ to that of the sodium bicarbonate, and thus *the concentration of the* $\mathrm{Pb}^{\cdot\cdot}$*-ions will be directly proportional to that of the free carbonic acid, and inversely proportional to the square of that of the sodium bicarbonate.*

This important theoretical deduction was experimentally verified by placing lead in contact with water containing 8·3 mgms. O_2, 35·3 mgms. NaHCO_3, and about 33 mgms. CO_2 per 1 litre, with the result that the amount of lead in solution was found to be about 1 mgm. per 1 litre, and thus slightly but distinctly greater than in the previous experiment in which there was no free carbonic acid present, and in which 0·6 mgm. Pb per 1 litre was taken up by the water.

In ordinary natural waters the phenomena are complicated by the simultaneous presence of other salts, especially chlorides and sulphates. Both PbCl_2 and PbSO_4 are considerably more soluble than the carbonate. On adding 71 mgms. $\mathrm{Na}_2\mathrm{SO}_4$ per 1 litre to the last artificial water mentioned above, it was found that the proportion of lead taken up was about tripled, being about 3 mgms. per litre. This increase must, of course, depend on the presence of PbSO_4 molecules in solution, and not on an increase in the concentration of the $\mathrm{Pb}^{\cdot\cdot}$-ions, which it was shown was already fixed by the concentrations of the carbonic acid and bicarbonate. Now by removing some of the free carbonic acid (*e.g.* by adding $\mathrm{Na}_2\mathrm{CO}_3$) the concentration of the $\mathrm{Pb}^{\cdot\cdot}$-ions will be diminished, and this will have the effect of also diminishing the amount of lead in solution due to the solubility of the PbSO_4, for the amount of undissociated PbSO_4 is dependent on the concentration of the $\mathrm{Pb}^{\cdot\cdot}$-ions, and if the latter be, through any cause, diminished, the amount of undissociated PbSO_4 must be diminished also, with the result that the total amount of lead passing into solution will be less. This was experimentally verified by using the same artificial water as in the last-mentioned experiment, excepting that by the addition of $\mathrm{Na}_2\mathrm{CO}_3$ the free carbonic acid was reduced to about 9·5 mgms. CO_2 per litre, and the NaHCO_3 consequently raised to about 128 mgms. per litre, with the result that the lead taken up amounted to only 1·3 mgm. per litre of water.

Experience has also shown that some waters act powerfully on lead when the pipes are charged intermittently, whilst the action becomes very much diminished if they are kept under constant pressure. The effect of pressure on the action ought, therefore, always to be specially determined (P. F. Frankland, J. Soc. Chem. Ind. 1889).

In investigating the action of water on lead, the water should either be put in contact with strips of the metal or placed in leaden pipes for a definite period of time, after which it should be removed and tested for lead *both in solution and suspension*, fresh portions of the water under examination are then placed in contact with the metal and again tested after a definite interval of time, this procedure being repeated a number of times. Thus it is often found that a water has a considerable initial action on the metal, but as the latter becomes coated with deposit, the action moderates and may practically cease altogether. Some waters, on the other hand, act continuously on the metal.

Some polluted waters have a very strong and continued action on lead (Riv. Pollut. Commiss. 6th Rep. 226), and in such cases the obvious remedy is the abandonment of the source.

It is worthy of note that hot water generally acts much more violently on lead than cold, and further that the lead dissolved in water is entirely removed by passage through any of the numerous forms of animal charcoal filters.

As regards the quantity of lead in water from which danger to health is to be apprehended, it is now generally admitted that water containing anything above one-twentieth grain of lead per gallon, or 0·07 part per 100,000, may, by continued use, produce mischief.

Of the action of water on zinc but little is known beyond the fact that many waters do act on it, and that it is therefore not to be recommended for the construction of cisterns, &c., in which drinking water is to be stored. The solution of the zinc takes place with special facility if metallic iron is also in contact with it (Heaton, Chem. News, 49, 85; P. F. Frankland, *ibid.* 115; Stevenson, *ibid.* 107).

Copper appears to be continuously acted on by water, especially if simultaneously in contact with air, and hence should not be used in connection with drinking water.

The action of water and other liquids on aluminium is now a matter of some importance owing to its use for domestic and industrial purposes (*see* An Investigation of Aluminium with Special Reference to its Suitability for the Construction of Brewery Plant, A. C. Chapman, J. Inst. Brewing, 1911). Although acted on by moist air the layer of oxide exerts a marked protection to further attack; alkalis and alkaline chlorides increase the tendency to corrosion. Chapman considers that it may be safely used for the construction of brewery plant, especially fermenting tuns and vessels intended for the treatment of chilled and filtered beers.

THE CHEMICAL ANALYSIS OF WATER.

As the qualitative analysis of the ingredients of water is of no practical importance, and involves no special methods, the quantitative examination will alone be considered here. In order that the analysis may be of any value, especially for sanitary purposes, it is of the greatest importance that the samples should have been collected with care.

Suspended matter. The suspended matter, if considerable in amount, should be separately determined, but if only present in minute quantity it is advisable to regard it as part of the dissolved matter, in which case it is necessary that the sample should be well shaken before taking out each portion for analysis, so that the suspended particles may be uniformly distributed. If it is decided to determine the suspended matter separately, the sample should be well shaken, and 250 or 500 c.c. measured out and passed through a filter previously dried at 100° and weighed. The matter on the filter is washed with distilled water, and dried at 100° until of constant weight. Some analysts prefer to dry at 105°, 110°, or even 120°, but in all cases the temperature should be specified. The filter and its contents are then incinerated in a coil of platinum wire and dropped into a weighed platinum crucible, gently ignited until free from organic matter, and then treated with a few drops of a solution of ammonium carbonate, and dried at 150°. The loss in weight represents organic matter and water of hydration. It is sometimes of importance to determine the proportion of carbon to nitrogen in the organic part of the suspended matter. For this purpose some of the suspended matter is collected on an ignited plug of asbestos or glass wool, transferred to a small flask, and boiled with 20 c.c. of sulphurous acid and some distilled water free from ammonia and organic matter, and then further treated, as in the determination of organic carbon and nitrogen, by the combustion process (*v.* p. 717). If the suspended matter has been thus separately determined, the remainder of the analysis should be performed on the water, after filtration through Swedish paper, rejecting the first 250 c.c. which pass through; or if the suspended matter completely settles on standing the clear water may be siphoned off. The suspended matter may, of course, in exceptional cases also have to be submitted to a complete mineral analysis, or examined for some special ingredient.

An ingenious method of determining minute traces of suspended matter has been devised by Dibdin (Analyst, 1896, 21, 2). In this method the volume of the moist suspended matter is measured in a capillary tube.

MATTERS IN SOLUTION.

Total solids. 250 or 500 c.c. of the water are evaporated to dryness in a weighed platinum dish on a water- or steam-bath, the dish being supported on a glass or porcelain, but not on a metallic, ring. The dish and residue are then dried until constant at 100°, 105°, 110°, 120°, or even at 180°. The residue may be further utilised for the determination of nitrates and nitrites by the mercury method (*v. infra*).

Ammonia. A measured volume of the water (varying from 100–1000 c.c., according to the proportion of ammonia present) is distilled in a capacious flask or retort connected with a Liebig's condenser, about 1 grm. of recently ignited sodium carbonate having been previously added. It is essential that the whole apparatus should have been carefully freed from ammonia immediately before use, which can be done by distilling some water in the apparatus until the distillate gives no reaction with Nessler solution. The remainder of the water in the flask or retort is then thrown away, and the measured quantity of the sample under examination introduced along with the sodium carbonate. The distillation should be carried on briskly, and the distillate collected in colourless glass cylinders of 50 c.c. capacity. If less than 500 c.c. has been used, this volume should be made up with distilled water free from ammonia before distillation. If the quantity of water has been well chosen, the whole of the ammonia will be found in the first three cylinders of the distillate, and in most cases it will all be contained in the first. The quantity of ammonia in each cylinder is estimated by adding 1 c.c. of Nessler solution, and comparing the coloration obtained with that similarly produced by known quantities of a standard solution of ammonium chloride, added to 50 c.c. of distilled water free from ammonia. The Nessler reaction is so delicate that by its means 1 part of NH_3 in 100,000,000 parts of water can be easily detected. The colour produced by more than 10–15 c.c. of a solution of NH_4Cl (containing 0·00001 grm. NH_3 per litre) is too deep for accurate comparison, and should one of the cylinders require more than this the determination must be repeated on a smaller volume of water. This may be generally avoided, however, by adding the Nessler solution to the second and third cylinders of distillate before the first, and if it is found that the second cylinder gives a colour requiring more than 5 c.c. of the above solution of ammonium chloride for its imitation the first cylinder should be diluted, and an aliquot part taken for testing with the Nessler reagent.

The Nessler solution is prepared by dissolving 62·5 grms. of potassium iodide in 250 c.c. of distilled water; set aside 10 c.c. of this, and run into the remainder a cold saturated solution of mercuric chloride until a permanent precipitate is formed, then add the above 10 c.c. of potassium iodide, which will cause its solution, after which very carefully add more of the mercuric chloride until a slight precipitate remains on stirring. Now add 150 grms. of potassium hydroxide dissolved in distilled water, and dilute the whole to 1000 c.c. After settling, decant the clear liquid into a bottle for use.

As the 'albuminoid ammonia' is commonly determined in one operation with the 'free' ammonia, the method of estimating the former will now be described, instead of considering it under the methods for determining organic matter, where it more properly belongs.

'Albuminoid ammonia' process. Whilst the determination of the free ammonia is being proceeded with as above, the solution of alkaline permanganate must be prepared for this process, as it is required immediately the free ammonia has passed over. The volume of the alkaline permanganate (for preparation *v.* below) taken must be at least one-tenth of the volume of the sample being distilled for ammonia, and it should not exceed that volume unless the water contains a very large amount of organic matter. The alkaline permanganate taken is then diluted with

four times its volume of distilled water, and boiled in a flask during the whole of the time that the distillation for free ammonia is going on as above, and when the latter is finished it is added to the water remaining in the distilling flask or retort (the whole volume in this must now be not less than 500 c.c.), and distillation is then continued until the distillate is free from ammonia. The distillate is collected and Nesslerised, as in the determination of free ammonia above. The ammonia thus evolved by distillation with alkaline permanganate is generally recorded as 'albuminoid ammonia' (*v.* p. 719). The alkaline permanganate solution is prepared by dissolving 200 grms. of potassium hydroxide and 8 grms. of pure potassium permanganate in 1100 c.c. of distilled water, then boiling the solution rapidly until concentrated to about 1000 c.c.

Chlorine. (*a*) *Mohr's method.* 50 or 100 c.c. of water are treated with a few drops of a solution of potassium chromate, and a standard solution of silver nitrate is then run in from a burette until the precipitate becomes of a faint but distinctly red colour. The water must be well agitated after each addition of the nitrate, the reaction depending upon the decomposition of the red silver chromate by dissolved chlorides with formation of silver chloride and soluble chromate. As soon as the last trace of chloride is precipitated as silver chloride, the red colour of the silver chromate makes its appearance. By using a solution of silver nitrate containing 2·3944 grms. per litre, the number of c.c. employed gives at once (if 50 c.c. of water have been taken) the parts of Cl per 100,000, whilst if 100 c.c. of water are taken the silver nitrate solution should be of double this strength.

Mohr's method cannot be employed if the water is acid, and if this is the case a given volume of the water should be boiled with an excess of pure calcium carbonate (free from chlorides), filtered, the filtrate made up to known volume, and the chlorine determined in a part of this. In the presence of reducing substances, much organic matter, sulphuretted hydrogen, and sulphites, the method is also inapplicable, and in such cases it is desirable to determine the chlorine gravimetrically, which should also be done if the proportion of chlorine is large.

(*b*) *Volhard's method.* 50 or 100 c.c. of the water are treated with an excess of decinormal silver nitrate, the mixture being well agitated so as to cause the silver chloride to settle in flakes; the latter is filtered off and washed, and then to the filtrate about ten drops of a cold saturated solution of iron-alum are added, and subsequently enough strong nitric acid (free from nitrous acid) to remove the colour of the ferric salt. Decinormal ammonium thiocyanate is then added from a burette, stirring well all the time, until the liquid acquires a light-yellow brown colour, which remains permanent on leaving the liquid at rest for about 10 mins. By deducting the number of c.c.'s of thiocyanate from that of the silver nitrate added, the remaining silver nitrate indicates the proportion of chlorine present in the water. The advantage of this method consists in its being applicable to acid liquids. The method depends upon there being no formation of red ferric thiocyanate until the whole of the silver in solution has been precipitated as thiocyanate (Annalen, 190, 24).

Nitrogen as nitrates and nitrites. A number of different methods have been devised for the determination of oxidised nitrogen; there are, however, only a few which have been largely adopted in practice, and such alone will be described here.

(*a*) *Crum's method.* This depends on the decomposition which nitrates and nitrites undergo when dissolved in strong sulphuric acid on being shaken up with mercury, and which leads to the evolution of the whole of the nitrogen as nitric oxide, the volume of which is then determined. The residue obtained in the estimation of the total solids (*see* p. 711) may be conveniently used for this determination also. This residue in the platinum or glass dish is repeatedly treated with a very small quantity of hot distilled water, which is brought into thorough contact with the residue by detaching the latter with a small glass rod covered with a piece o india-rubber. The aqueous extracts, which should in all not exceed about 10 c.c., ar passed through a small filter and collected in a little beaker. This aqueous extract, containing all the soluble salts in the water residue, is evaporated nearly to dryness on a water-bath after which it is dissolved again in a minimum quantity (1 or 2 c.c.) of water, and introduced into a Lunge nitrometer (Ber. 11, 434); the beaker is repeatedly rinsed with a few drops of hot water, and these rinsings added to the nitrometer. The beaker is then further rinsed with pure strong sulphuric acid (free from oxides of nitrogen), and this also is transferred to the nitrometer. About 1½ volumes of sulphuric acid must in all be used to 1 volume of aqueous extract. If the water contains soluble carbonates there will be an evolution of carbon dioxide when the sulphuric acid mixes with the aqueous extract; the gas should be allowed to collect *without shaking the tube*, and should then be expelled. The contents of the nitrometer tube are now violently agitated with the mercury, and then in the course of a minute or so the evolution of nitric oxide will commence, and the agitation should be continued as long as any gas continues to come off. If the water contains a considerable quantity of chlorides some hydrogen chloride may have been given off with the nitric oxide, but this may be removed by admitting a little water into the nitrometer. When the gas has cooled to the temperature of the air, its volume is measured at atmospheric pressure. The determination is rendered more accurate, especially if the quantity of nitrates and nitrites is only small, by measuring the nitric oxide in Frankland's gas apparatus, in which case the decomposition with mercury and sulphuric acid is effected in a small tube standing in a mercury trough, the evolved nitric oxide being then transferred to the gas apparatus (*see* Sutton's Volumetric Analysis). This method, which is by far the most convenient for ordinary water analysis, becomes inapplicable in the presence of very large quantities either of organic matter or of chlorides.

(*b*) *Methods of Schulze-Tiemann, and of Schlösing-Reichardt,* depend upon the decomposition of nitrates and nitrites by ferrous chloride and hydrochloric acid, and the measurement of the evolved nitric oxide. Of these methods, which closely resemble each other, the former, as the more convenient, need be alone considered here.

100–500 c.c. of the water are concentrated by evaporation to about 50 c.c., which are then introduced into a flask of about 150 c.c. capacity, provided with an india-rubber stopper, perforated by two narrow pieces of glass tubing, of which one (A) extends about an inch into the flask, and is constricted below, whilst the other (B) only just penetrates the stopper; the tube (B) is externally connected by means of a short piece of india-rubber tubing provided with a pinch-cock, with a delivery tube dipping into a trough containing 10 p.c. caustic soda solution previously boiled to expel air. The tube (A) is also connected with india-rubber and pinch-cock to another piece of glass tubing, which is allowed to hang vertically downwards. The water in the flask is vigorously boiled with the pinch-cocks open until the air is completely expelled by the steam, then the pinch-cock on (B) is closed whilst that on (A) is left open until the volume of water in the flask is reduced to about 10 c.c.; this pinch-cock is then also closed, and the flame removed from beneath the flask. The glass tube attached to (A) is carefully filled with water up to the pinch-cock; 15–20 c.c. of a saturated solution of ferrous chloride are introduced into the flask, in which there is now a partial vacuum, by siphoning from a small beaker through (A), the pinch-cock being temporarily opened, and about an equal quantity of strong hydrochloric acid is made to follow in the same manner into the flask. The flask is now carefully heated, and when the internal pressure rises the pinch-cock on (B) is opened, and the evolved gas allowed to pass through the delivery tube into a measuring tube filled with the 10 p.c. caustic soda solution standing in the trough. The heating of the flask is continued until the volume of gas in the measuring tube ceases to increase. The measuring tube is transferred to a tall glass cylinder full of water, and after the gas has acquired the temperature of the room the volume is measured at the atmospheric pressure, a correction being of course made for the tension of aqueous vapour.

This method is specially applicable to the case of water containing excessive quantities of organic matter and chlorides (Ber. 1873, 1041; Tiemann and Gärtner's Untersuchung d. Wassers, 170).

For Schlösing-Reichardt's method, *v.* Zeitsch. anal. Chem. 1870, 24, or Tiemann and Gärtner's Untersuch. d. Wassers, 175.

(*c*) ***The aluminium and zinc-copper couple methods*** depend upon the conversion by nascent hydrogen of the oxidised nitrogen in the water into ammonia, and estimation of the latter by Nessler solution.

Aluminium method. 100 c.c. of the water are introduced into a flask together with 10 c.c. of caustic soda solution free from nitrates and nitrites, the mixture being boiled until it is reduced to about one-fourth of its volume. It is then diluted to about its original bulk with distilled water free from ammonia, and a piece of aluminium foil, about 2 ins. square and wrapped round a piece of glass rod, is dropped into the flask, which is then fitted with a stopper and small U-tube containing glass beads moistened with hydrochloric acid free from ammonia. After the evolution of hydrogen has continued for about 6 hours, the glass beads and washings of the U-tube are transferred to the liquid in the flask, the latter is then attached to a Liebig's condenser, and the ammonia determined by distillation and Nesslerising in the ordinary way (*see* p. 711). According to Tiemann and Gärtner (Untersuchung d. Wassers, 208), only the equivalent of 72–90 p.c. of the nitric acid is thus recovered as ammonia.

Zinc-copper couple method. The residue obtained in the determination of 'total solids' is extracted with about 25 c.c. of hot distilled water, and this is boiled down with a fragment of recently-ignited pure lime about the size of a hemp-seed to one-fourth of its bulk. This liquid, together with the washings of the dish containing the residue, is transferred through a stoppered funnel into an eight-ounce Wurtz flask, attached to a Liebig's condenser, and containing the requisite amount of the zinc-copper couple. The distillation is carried on until the greater part of the water has passed over, after which hot distilled water is repeatedly run into the flask and the distillation continued until about 100 c.c. of distillate have been collected; the latter is then 'Nesslerised' in the ordinary way (Thorpe, Chem. Soc. Trans. 1873, 541). According to Tiemann and Gärtner, from 88 to 95 p.c. of the nitric acid is thus obtained.

In the writer's laboratory the process is carried out as follows: A stoppered bottle (about 200 c.c. capacity) is loosely filled with strips of zinc, which, after cleaning with dilute sulphuric acid, are covered with copper sulphate solution (1 p.c.). The copper-coated strips are repeatedly washed with distilled water, and finally with the water under examination, care being taken not to detach the copper film. The bottle is then completely filled with the sample of water and a crystal of oxalic acid is added, and the bottle, loosely stoppered, is allowed to stand over night. A definite volume is withdrawn by means of a pipette, and this is distilled with a suitable volume of ammonia-free water in the ammonia apparatus as usual, a small quantity of ignited sodium carbonate being added. Before withdrawing the water from the bottle for distillation, a small quantity should be tested for nitrite to ensure that the reduction to ammonia is complete. Waters containing free or saline ammonia must have this distilled off before being placed in contact with the zinc-copper couple.

A rapid method of estimating nitrates in water is due to Harrow (Chem. Soc. Trans. 1891, 320), depending on the reduction to nitrite by zinc-dust and estimation of the nitrous acid by sulphanilic acid and *a*-naphthylamine (Griess' test). This reagent is prepared by dissolving 1 grm. of *a*-naphthylamine, 1 grm. sulphanilic acid, and 25 c.c. strong hydrochloric acid in about 200 c.c. distilled water; boil with a small quantity of animal charcoal, filter, and make up to 500 c.c. The process is conducted thus: 50 c.c. of the water are placed in a beaker of 100 c.c. capacity, and in three similar beakers 50 c.c. of three standard solutions of potassium nitrate, containing (1) 1·

part N, (2) 0·1 part N, (3) 0·01 part N per 100,000; to each beaker 10 c.c. of the above test-solution are added, and afterwards a very small quantity (7–8 mg.) of zinc-dust. If nitrate is present in the water a pink colour appears, which must be compared with that yielded by the three standard solutions after 15 mins. This gives an approximate idea of the amount of nitrate present, whilst in order to obtain an accurate result the water must be diluted until the colour produced is almost identical with that given by one of the standards. The results appear to be accurate, but it is especially necessary to avoid the addition of large quantities of zinc-dust, which would decolorise the solution.

(*d*) *The indigo method* differs from those previously described in being a simple volumetric method depending upon the decolorising action of nitric acid on indigo solution. The results are only accurate when the greatest uniformity is preserved in the conditions under which the experiments are made—the process is, in fact, entirely empirical. It may be carried out as follows: 25 c.c. of the water are mixed with 50 c.c. of pure strong sulphuric acid; a dilute solution of indigo is then immediately added from a burette, shaking the whole time, until the solution acquires a bluish-green colour. In a second experiment nearly the whole volume of indigo which was found necessary in the first experiment is added at once, and the blue colour is then obtained by further small additions, and in this manner, by shortening the time taken in the titration, a more accurate result, generally higher than in the preliminary experiment, is obtained. The solution of indigo must be standardised under precisely similar conditions by means of a solution of potassium nitrate of known strength. The indigo solution should be chosen of such strength that 6–8 c.c. correspond to 0·001 grm. N_2O_5; and if 25 c.c. of the water contains more than 0·003–0·004 grms. N_2O_5, it should be diluted before a final titration is made. The method is only suitable for use by an operator in continual practice (Warington, Chem. Soc. Trans. 1879, 578; Water Analysis, E. Frankland, 31). The results are too low if there is a large amount of organic matter in the water.

The methods described above do not distinguish between nitrous and nitric acids. Indeed, the indigo method is altogether unreliable in the presence of any notable proportion of nitrous acid, as is also Crum's method, should it be necessary to allow any carbon dioxide to escape before shaking with mercury (*see* p. 712). As nitrous acid is, however, generally only present in natural waters in minute traces, these difficulties do not frequently arise, and the nitrous acid may be most conveniently estimated by colorimetric methods, of which there are several in vogue. Of these may be mentioned:

(*a*) *Preusse-Tiemann's method,* depending upon the production of Bismarck brown when an acid solution of a nitrite acts upon *m*-phenylenediamine. 100 c.c. of the water are placed in a colourless glass cylinder, 1 c.c. of dilute sulphuric acid (1 : 3) is added, and then 1 c.c. of solution of *m*-phenylenediamine (5 grms. in 1000 c.c. distilled water, decolorised if necessary with animal charcoal); if the colour appears in less than 1 or 2 mins. the experiment must be repeated with a smaller quantity of water, in each case diluted, however, to 100 c.c. The coloration is then imitated under precisely similar conditions with a standard solution (the standardisation can be effected either by the potassium permanganate, or, better, by the urea method) of potassium or sodium nitrite. The final tint is not arrived at until the mixture in the glass cylinder has stood for 20–25 mins., which is the great drawback of the process (*see* also Warington, The Detection of Nitric and Nitrous Acids, Chem. News, 1885, 51, 39).

A preferable method (Zambelli, Chem. Soc. Abstr. 1887, 533) consists in adding to the water a few drops of a saturated solution of sulphanilic acid in dilute sulphuric acid, then a few drops of a saturated aqueous solution of phenol, after which the mixture is rendered alkaline with ammonia. The presence of nitrous acid is indicated by the appearance of a coloration, varying from faint yellow to intense reddish yellow, according to the quantity of nitrous acid present. The author claims that this method is capable of revealing the presence of 1 part of nitrous nitrogen in 40,000,000 parts of water. It has the great advantage that the reagents employed are permanent in solution.

For larger quantities of nitrous acid, as also for the standardisation of solutions of sodium and potassium nitrite, the urea method devised by the writer is to be recommended (Chem. Soc. Trans. 1888, 364).

Hardness. The determination of the hardness of a water consists in empirically ascertaining the amount of soap which has to be destroyed by a given volume of the water before a lather can be obtained, and expressing this in terms of the amount of calcium carbonate which must be dissolved in the same volume of water to destroy the same amount of soap. Accurate results can only be obtained by preserving uniformity in the conditions of experiment.

50 c.c. of the water are measured into an 8-oz. stoppered bottle, which is then violently agitated and the air sucked out by means of a glass tube to remove any carbon dioxide which may be given off by the water. A standard solution of soap (*v. infra*) is then added in diminishing quantities *not exceeding* 0·5–0·10 c.c. *at a time, even at first,* violently shaking after each addition, until the froth produced remains unbroken over the surface for a period of 5 mins. when the bottle is placed at rest on its side. The quantity of calcium carbonate corresponding to the volume of soap solution employed can then be ascertained by reference to the empirical table shown opposite.

In performing the titration as above, the experienced operator is guided by the ear as well as by the eye, for the sound produced on shaking serves to indicate how the reaction between the hardening constituents of the water and the soap is progressing, for as this approaches completion the sound becomes softer, and when an excess of soap has been added the agitation is all but noiseless.

In the case of waters requiring more than 16 c.c. of soap solution for the 50 c.c. of water, it is necessary to take a smaller volume of the

Table of hardness in parts per 100,000, 50 *c.c. of water being used.*

C.c. of soap solution	$CaCO_3$ per 100,000	C.c. of soap solution	$CaCO_3$ per 100,000	C.c. of soap solution	$CaCO_3$ per 100,000
·7	0·00	5·9	7·29	11·0	14·84
·8	·16	6·0	·43	·1	15·00
·9	·32	·1	·57	·2	·16
1·0	·48	·2	·71	·3	·32
·1	·63	·3	·86	·4	·48
·2	·79	·4	8·00	·5	·63
·3	·95	·5	·14	·6	·79
·4	1·11	·6	·29	·7	·95
·5	·27	·7	·43	·8	16·11
·6	·43	·8	·57	·9	·27
·7	·56	·9	·71	12·0	·43
·8	·69	7·0	·86	·1	·59
·9	·82	·1	9·00	·2	·75
2·0	·95	·2	·14	·3	·90
·1	2·08	·3	·29	·4	17·06
·2	·21	·4	·43	·5	·22
·3	·34	·5	·57	·6	·38
·4	·47	·6	·71	·7	·54
·5	·60	·7	·86	·8	·70
·6	·73	·8	10·00	·9	·86
·7	·86	·9	·15	13·0	18·02
·8	·99	8·0	·30	·1	·17
·9	3·12	·1	·45	·2	·33
3·0	·25	·2	·60	·3	·49
·1	·38	·3	·75	·4	·65
·2	·51	·4	·90	·5	·81
·3	·64	·5	11·05	·6	·97
·4	·77	·6	·20	·7	19·13
·5	·90	·7	·35	·8	·29
·6	4·03	·8	·50	·9	·44
·7	·16	·9	·65	14·0	·60
·8	·29	9·0	·80	·1	·76
·9	·43	·1	·95	·2	·92
4·0	·57	·2	12·11	·3	20·08
·1	·71	·3	·26	·4	·24
·2	·86	·4	·41	·5	·40
·3	5·00	·5	·56	·6	·56
·4	·14	·6	·71	·7	·71
·5	·29	·7	·86	·8	·87
·6	·43	·8	13·01	·9	21·03
·7	·57	·9	·16	15·0	·19
·8	·71	10·0	·31	·1	·35
·9	·86	·1	·46	·2	.51
5·0	6·00	·2	·61	·3	·68
·1	·14	·3	·76	·4	·85
·2	·29	·4	·91	·5	22·02
·3	·43	·5	14·06	·6	·18
·4	·57	·6	·21	·7	·35
·5	·71	·7	·37	·8	·52
·6	·86	·8	·52	·9	·69
·7	7·00	·9	·68	16·0	·86
·8	·14				

water and dilute to 50 c.c. with boiled distilled water. The presence of magnesia salts is indicated in the soap test by the formation of a characteristic light curd, and also by the premature formation of a lather, which again disappears on the further addition of soap solution and shaking. If these signs are exhibited, only such a volume of water should be taken as, when diluted to 50 c.c., requires not more than 7 c.c. of the soap solution; indeed, it is a very good practice to invariably dilute waters so that not more than 7 or 8 c.c. of soap solution are required. In the presence of magnesia salts the results are always less accurate, and, unless great care is exercised, may become wide of the truth.

Permanent hardness. The permanent hardness is most conveniently determined by taking a small flask with a *very short neck* (the Erlenmeyer shape is very suitable), and adding the water to it until a definite weight (*e.g.* 250 grms.) has been made up. The water is then maintained in gentle ebullition for exactly half-an-hour, and, after cooling, the weight is again made up to the original by the addition of boiled distilled water, the soap titration being then performed on a measured portion of this, as described above.

Some analysts prefer to take a given volume of water and restore the volume after boiling, then removing the precipitated carbonates of lime and magnesia by passing through a dry filter.

The *standard solution of soap* is prepared as follows. A cake of Castile soap is scraped with a knife, and about 7 grms. of the shavings are dissolved in 500 c.c. of a mixture of 2 vols. of methylated spirit with 1 vol. of distilled water. Filter off the insoluble matter, and dilute the soap solution with half its volume of water. A portion of this solution is then further carefully diluted with a mixture of 2 vols. methylated spirit and 1 vol. water until 7·8 c.c. are required to form a permanent lather with a mixture of 25 c.c. of the standard calcium chloride solution (prepared by dissolving 0·2 grm. of Iceland spar in dilute hydrochloric acid, and, after driving off excess of acid on the water-bath, making up to 1000 c.c. with distilled water) and 25 c.c. of distilled water.

Poisonous metals. Of these the only ones which are of practical importance in water analysis are lead, zinc, copper, arsenic, and barium. As they are generally present in only very minute proportions, it is necessary to evaporate large volumes (5 litres and upwards) of water in order to obtain gravimetric determinations in the ordinary way; but the following special methods may be generally employed.

For *lead*, take 100 c.c. of the water, acidify with a few drops of acetic acid, and then add about 5 c.c. of a saturated solution of sulphuretted hydrogen. The colour produced is imitated by adding a known quantity of a standard solution of a lead salt to 100 c.c. of distilled water. Even such small proportions as 0·03 part Pb per 100,000 should be invariably recorded. (For the standard solution of lead, dissolve 0·1831 grm. crystallised normal lead acetate in 1000 c.c. distilled water; 1 c.c. = 0·0001 Pb.)

For *copper*, the same colorimetric method may be employed as for lead, using for comparison a solution of copper sulphate containing 0·0001 grm. Cu in 1 c.c. (0·3929 grm. crystallised copper sulphate per litre). In the absence of iron a very delicate colorimetric method may be employed, based upon the reaction between copper salts and potassium ferrocyanide, the water being acidified with hydrochloric acid, whilst in the presence of iron the blue coloration produced by ammonia may be used.

The presence of *zinc* is generally indicated by the gradual formation of a film of carbonate on the surface of the water when the latter is exposed to the air. Some of this film ignited on platinum foil should leave a residue, which is yellow when hot and white on cooling. The quantity of the zinc may be approximately determined, in the absence of other heavy metals, by acidifying 100 c.c. of the water with dilute hydrochloric acid, and then adding a solution of potassium ferrocyanide. The white turbidity produced is then compared with that obtained from a known quantity of a standard solution of a zinc salt (Snijders, Ber. 1878, 939).

Arsenic is best detected and estimated by Marsh's test; 500 c.c. of the water are rendered slightly alkaline with caustic soda or potash free from arsenic, and evaporated to dryness. The residue is extracted with strong hydrochloric acid, and the liquid introduced into a Marsh's apparatus. The gas is passed through a small U-tube containing pumice soaked in solution of lead acetate, and then through a piece of combustion tube constricted in the middle, where it is heated to redness. The passage of gas through the heated tube is continued for an hour, although nearly all the arsenic is liberated in 5 or 10 mins. The metallic ring formed is compared with a number of standard rings similarly obtained with known quantities of arsenic. A blank experiment must invariably be performed previously, to control the purity of the chemicals employed.

Barium may be detected and determined by concentrating a considerable volume of the water, acidifying with hydrochloric acid, and after filtering, if necessary, adding a solution of calcium sulphate. The barium sulphate precipitated is then collected and weighed in the ordinary manner.

Iron can generally be estimated colorimetrically by means of ferrocyanide or thiocyanate. Its determination is frequently of importance in waters used for industrial purposes.

In the ferrocyanide method, the water residue is dissolved in hydrochloric acid and diluted to 100 c.c. Of this 10 c.c. are transferred to a 100 c.c. cylinder; add 1 c.c. of strong nitric acid, dilute to 100 c.c., stir, and then add 1 c.c. of potassium ferrocyanide solution and mix well. The colour produced is compared with that obtained from a standard iron solution, but the same quantity of nitric acid must be present in each case (Sutton, Volum. Analys. 6th ed. 194; *v.* also Carter Bell, J. Soc. Chem. Ind. 8, 175).

In the thiocyanate method, two 100 c.c. cylinders are taken, and into each 5 c.c. of dilute hydrochloric acid (1 : 5) and 5 c.c. of dilute nitric acid (1 : 5), together with 15 c.c. of thiocyanate solution, are poured; then introduce a measured volume of the liquid to be tested into the one cylinder, and after filling up both cylinders to the mark with distilled water, imitate the red colour obtained with the liquid under examination by running in a standard solution of iron from a burette into the other cylinder. In this way one part of iron is said to be recognisable in fifty millions of water (Thompson, Chem. Soc. Trans. 1885, 493).

Determination of organic matter. A number of processes have been devised for the determination either of the whole or part of the organic substances present in water. Of those which lay claim to discovering the whole of these organic materials, none is entitled to any confidence, whilst even those which attempt to determine a part, or to indirectly obtain a comparative measure of the organic matter, are also open to objections on the score of accuracy. Only those methods more commonly in use by water analysts will be described here.

(1) ***Methods depending on the reduction of potassium permanganate.***

(*a*) *Kubel's process.* In this the reduction is effected in acid solution. 100 c.c. of the water are placed in a flask of about 300 c.c. capacity and treated with 5 c.c. dilute sulphuric acid (1 : 3), and then with such a quantity of standard dilute permanganate (equivalent to centinormal oxalic acid) that the liquid is of a strong red colour. The mixture is then boiled for 10 mins., and the excess of permanganate added must be such that the colour is not discharged in this operation. 10 c.c. of centinormal oxalic acid are now added, and into the resulting colourless liquid standard permanganate is then run in until a faint red colour is obtained. The amount of oxygen consumed by the organic matter in the water can then be calculated.

(*b*) *Schulze's process.* In this the reduction is commenced in an alkaline and completed in an acid solution. 100 c.c. of the water are placed in a flask of about 300 c.c. capacity, 0·5 c.c. caustic soda solution (1 : 2) are added, as well as 10–15 c.c. of standard dilute permanganate (equivalent to centinormal oxalic acid). The liquid is boiled for 10 mins., allowed to cool to 50° or 60°C. and then 5 c.c. of dilute sulphuric acid (1 : 3) and 10 c.c. of centinormal oxalic acid are added, the liquid being shaken and gently warmed until the colour has quite disappeared. Then the standard dilute permanganate is run in until a faint red colour, remaining permanent for at least 5 mins., is obtained. The oxygen consumed by the organic matter of the water is then calculated.

(*c*) *Forchhammer process.* This resembles Kubel's method, inasmuch as the reduction of the permanganate is effected in an acid solution, but the temperature employed, instead of being defined, is that of the air of the laboratory.

Two flasks are carefully cleaned and into one 250 c.c. of the water, into the other 250 c.c. of distilled water, are introduced. To each 10 c.c. of dilute sulphuric acid (1 : 3) and 10 c.c. of standard permanganate (containing 0·395 grm. per litre or 0·001 grm. available oxygen in 10 c.c.) are added, and the mixture is allowed to stand for three hours. At the end of this time the excess of permanganate remaining is determined by adding two drops of potassium iodide (1 : 10) to each flask, and then running in a standard solution of sodium thiosulphate (1 grm. per litre) until the whole of the free iodine is removed, a drop of clear starch solution being added at the close of the operation. The amount of permanganate destroyed in the blank experiment must of course be deducted from that destroyed in the case of the water, and from the difference the oxygen consumed by the organic matter of the water can be calculated (Tidy, Chem. Soc. Trans. 1879, 66).

In this country it is now almost the invariable custom of water analysts to allow the acid permanganate to act for 4 hours at 80°F. (26·7°C.); Thorpe (Metropolitan Water Reports, 1904) has also used 1 hour at 122°F. (50°C.), under which conditions a larger amount of oxygen is consumed.

It must be pointed out that in these several methods depending on the reduction of permanganate, the results are only comparative for the same kind of organic matter, a given weight of organic carbon in different kinds of water consuming different quantities of oxygen from permanganate under the same conditions. Thus it has been found that for surface waters, such as those of the rivers Thames and Lea, by multiplying the oxygen consumed in the Forchhammer process by the factor 2·38, the proportion of organic carbon (as determined by combustion) is approximately obtained, whilst in the case of deep well water the factor which must be employed is 5·8 (Woodland Toms).

Again, all these methods are affected by the presence of nitrites, ferrous salts, and larger quantities of ammonia compounds, all of which exercise a reducing action on permanganate. By determining the nitrous acid, a correction can be made for this, whilst the ferrous can generally be converted into ferric iron by shaking up the water several times in a half-filled bottle previously to the oxidation with permanganate; and the error due to ammonium salts is so small that it can generally be neglected (even one part NH_3 per 100,000 has no appreciable reducing effect) (Preusse and Tiemann, Ber. 12, 1906).

(2) *Determination of organic carbon by oxidation of organic matter with potassium dichromate and sulphuric acid* (Wolff, Degener, and Herzfeld). 500–1000 c.c. of the water are introduced into a capacious retort, the neck of which is drawn out and bent downwards and is connected with a Liebig's condenser. This arrangement enables the retort to be turned upwards and the condenser downwards, thus preventing any loss by spurting during distillation, which is carried on until 250–700 c.c. (according to the volume of water employed) have passed over. The distillate is submitted to Kubel's method (*v. supra*) to ascertain whether any volatile organic matters are present. Alkaline waters should be saturated with carbon dioxide, and acid waters carefully neutralised with sodium carbonate before the above distillation. The water remaining in the retort is evaporated down to 15 c.c. in a glass dish on a water-bath, the access of dust being carefully avoided. This concentrated liquid is introduced into a flask of 250–300 c.c. capacity, and the dish and retort are rinsed with 10 c.c. of dilute sulphuric acid (1 : 3), these rinsings being also added to the water in the flask. The decomposition of carbonates caused by the addition of this acid is completed by heating to 50°C. and shaking, and the evolved carbon dioxide completely displaced by air. After cooling the flask and its contents, 10 grms. of finely-powdered potassium dichromate are added, and the flask is then attached to the remainder of the apparatus. An india-rubber stopper with three holes is placed in the flask; through one hole passes a thermometer dipping into the liquid, through a second passes nearly to the bottom of the flask the tube of a bulb-funnel (A) provided with a stopcock, whilst through the third passes the bent tube of an inverted Liebig's condenser (B). The upper extremity of the condenser (B) is connected with two U-tubes (C and D) filled with fused calcium chloride, whilst between these is a third U-tube (E) containing coarsely-powdered antimony. Of these, C and D are intended to absorb the moisture passing the condenser, and the intermediate one, E, to retain any chlorine. Following on these tubes is a set of weighed potash-bulbs (F) for the absorption of carbon dioxide, and these bulbs are, of course, protected from ingress of air on the other side by means of a calcium chloride tube, which can be attached to an aspirator at the close of the experiment. The apparatus having been thus put together, 50–60 c.c. of diluted sulphuric acid (3 : 2) are gradually added through the stoppered funnel (A). During the first half-hour the temperature is kept at 50°–55°C., whilst during the second half-hour it is gradually raised to boiling, which is maintained from 5–10 mins. The aspirator is then attached, the air which enters by the funnel (A) having been previously freed from carbon dioxide by bubbling through caustic potash. The increase in weight of the potash bulbs (F) gives the weight of carbon dioxide evolved, from which the carbon itself can be calculated (Ber. 1886, 2618; Tiemann-Gärtner, Untersuch. d. Wassers, 247).

For a somewhat similar method of determining organic carbon in which permanganate is used instead of dichromate, *see* Blair, Organic Analysis of potable Waters, Churchill, 1891, 83. The method appears worthy of more extended trial.

(3) *Determination of organic carbon and nitrogen by combustion.* (*a*) *Frankland and Armstrong's process* (Chem. Soc. Trans. 6, 77). This method, which is unquestionably the most rational and exact, has been adopted to a comparatively limited extent by water analysts in consequence of the special apparatus and manipulative skill which it entails. The method will be only described in outline here, and for full particulars the reader is referred to Sutton's Volumetric Analysis, whilst for a critical survey of the methods employed in the organic analysis of water he should not fail to consult Mallet, Report of the United States National Board of Health, 1882.

The process is divisible into three parts: (1) the evaporation of the water, (2) the preparation and combustion of the residue thus obtained, and (3) the measurement of the gases evolved in the combustion.

For the *evaporation*, from 100 c.c. (in the case of sewage and highly-polluted waters) to 1000 c.c. (in the case of very pure waters) are measured into a clean flask, 20 c.c. of a saturated solution of sulphurous acid being added together with a drop of a solution of ferric chloride; the liquid is then rapidly boiled for a few seconds. This treatment secures the decomposition of carbonates, nitrates and nitrites, whilst any ammonia is fixed by the sulphurous acid, and this ammoniacal nitrogen, which has been previously determined, must be deducted from the total amount of nitrogen obtained in the combustion. The water is now rapidly cooled, and the evaporation commenced in an apparatus specially designed for the purpose. This consists of a nearly hemispherical glass dish about 4 ins. in diameter and without a lip. It is floated in a shallow copper basin heated below by a water-bath provided with constant feed, and on the flange of this copper basin there rests a truncated conical ring, constructed of lead or copper, and about 3 ins. in height, whilst upon a flange at the top of this again rests a tall glass shade about 12–18 ins. in height. The water for evaporation is placed in a flask which is provided with a delivery tube of special construction ground on to its neck, and which serves, when the flask is turned upside down, to maintain the water at a constant level in the glass dish in which the evaporation is proceeding, for this delivery tube is made to pass through a notch in the truncated conical metal ring, just beneath the glass shade which the latter supports, and delivers into the centre of the glass dish within. In the writer's laboratory, the evaporation of 500 c.c. of water is found to take from 10–12 hours. The evaporation should be continued until the residue is quite dry, and if the water contains only a small amount of total solids it is advisable to add a little ignited calcium phosphate to the dish before commencing the evaporation. In the analysis of sewage, or waters containing much ammonia and *no nitrates or nitrites*, it is advantageous to use 10 c.c. of a solution of metaphosphoric acid (1 : 10) instead of the sulphurous acid, as ammonium phosphate loses much less ammonia during evaporation than ammonium sulphite. A little ignited calcium phosphate should also be added to dry the residue in this case. But if there are no nitrates and nitrites and much ammonia, the more satisfactory, although more laborious, plan is to use a little ignited borax instead of the sulphurous or metaphosphoric acid. In this way the ammonia is completely dissipated on evaporation, and as no correction has, therefore, to be applied to the organic nitrogen found, the result is more correct. But as boric acid does not entirely decompose carbonates the accuracy of the organic carbon found by this method may be seriously affected, and it is advisable to make a separate determination of the carbon in a second experiment in which the sulphurous acid method is employed. Unless this method be adopted the results for organic nitrogen in the presence of much ammonia are nearly sure to be highly inaccurate.

If the water contains more than 0·5 part per 100,000 of nitrogen as nitrates and nitrites, the 20 c.c. of sulphurous acid employed above may not improbably prove insufficient for their complete destruction, and in the case of such waters the residue in the dish should be further treated with 10 c.c. of sulphurous acid, this evaporated off, and if the amount of nitric or nitrous nitrogen exceed 1 part per 100,000 this treatment of the residue with further quantities of sulphurous acid may be repeated twice or three times to secure complete destruction of the nitrates and nitrites.

The *preparation and combustion of the residue* thus obtained is effected by thoroughly mixing with the latter in the dish a small quantity of finely divided and carefully ignited copper oxide. This is then completely transferred a narrow piece of combustion tubing about 18 ins. long and sealed at one extremity. The dish is again rinsed with a little fine oxide, and this also transferred to the tube. Coarse and carefully ignited oxide of copper (preferably from wire) is then introduced to a depth of about 10 ins., whilst the fine oxide previously introduced will occupy about 2 ins. Upon the stratum of coarse oxide follows a copper gauze cylinder 3 ins. in length, and then another layer of coarse oxide about 1 in. long. The open extremity of the tube is now drawn out over the blowpipe, so that it can be connected with a Sprengel mercury pump. The tube is completely exhausted, and the combustion performed *in vacuo* in the ordinary way, the evolved gases being then drawn over by the pump and collected in a test tube filled with mercury and placed over the lower open extremity of the fall tube in the trough below.

The *volumetric measurement of the gases* (consisting of carbon dioxide, nitrogen, and possibly also nitric oxide and sulphur dioxide) collected as above is carried out in the Frankland gas apparatus, which admits of the measurement of very minute quantities of gas. Three measurements only are necessary. In the first place the gas is treated with a few drops of a saturated solution of potassium dichromate to absorb any sulphur dioxide that may be present. The volume of the gas is then accurately measured, after which it is treated with a few drops of strong caustic potash, which rapidly removes the carbon dioxide, after which the volume of the remaining gas is again carefully ascertained. The residual gas now consists of nitrogen, with possibly a little nitric oxide. It is mixed with a bubble of pure oxygen in order to convert any nitric oxide into nitrous and nitric acids, which are immediately absorbed by the caustic potash present, and then, on adding a drop or two of solution of pyrogallic acid, the excess of oxygen is absorbed and the remaining gas, which consists of nitrogen, is carefully measured. The diminution in volume effected by the caustic potash in the first instance obviously represents the carbon dioxide, whilst the final volume of residual gas, together with one-half of the contraction resulting from the addition of oxygen and pyrogallic acid, represent the total volume of nitrogen. From these volumes the weights of carbon and nitrogen respectively can be calculated. As already pointed out, if sulphurous or metaphosphoric acid has been used in the evaporation, and ammonia is present in the water, the ammoniacal nitrogen (subject to an empirical correction for loss of ammonia during evaporation) has to be subtracted from the total nitrogen found by combustion. A small correction (ascertained by blank experiments made from time to time with the reagents employed in the evaporation and combustion) has also to be applied to the carbon and nitrogen thus determined.

For *Dupré and Hake's method*, *see* Chem. Soc. Trans. 1879, 159.

In *Dittmar and Robinson's method* of determining organic carbon, the gases proceeding from the combustion tube are first passed through a U-tube containing a solution of chromic acid in 60 p.c. sulphuric acid to absorb moisture and sulphurous acid (the water is evaporated with sulphurous acid for the preparation of the residue), the carbon dioxide being absorbed in a weighed soda-lime tube (Chem. News, 1877, 36, 26). A method of determining organic nitrogen has also been devised by Dittmar and Robinson, and is described below.

(4) *Methods for determination of organic nitrogen only.* Of these the most common one in use is the well-known

(*a*) '*Albuminoid ammonia*' *process* of Wanklyn, Chapman, and Smith (Chem. Soc. Trans. 1867, 591), which does not yield the whole, but only very variable proportions, of the organic nitrogen in different nitrogenous organic substances, although in the case of some —such as leucine, aspartic acid, tyrosine, &c. —which frequently appear as decomposition products of albuminous matters, nearly the whole of the nitrogen is obtained as ammonia (Preusse and Tiemann, Ber. 12, 1906; Mallet, U. S. National Board of Health Report, 1882).

The method has already been described on p. 711.

(*b*) *Dittmar and Robinson's process.* In this process the residue, obtained in the same way as for the combustion process, is heated with fused caustic soda, or soda and baryta, in a copper or silver boat placed in a combustion tube in a current of hydrogen, the evolved ammonia being absorbed by very dilute hydrochloric acid, which is subsequently 'Nesslerised' (Chem. News, 1877, 36, 26). The results are accurate, and coincide with those obtained by the combustion process of Frankland and Armstrong.

(*c*) *Kjeldahl's process.* This well-known and now much-employed method for determining organic nitrogen was adapted for use in water analysis by Drown and Martin (Chem. News, 59, 272). It appears to give accurate results uninfluenced by the presence of nitrates and nitrites in such quantities as are found in ordinary waters, 500 c.c. of the water are placed in a round-bottomed flask of about 900 c.c. capacity; the volume is then reduced to about 200 c.c. by boiling, and to this, after cooling, add 10 c.c. of pure concentrated sulphuric acid. The mixture is then cautiously boiled, with the flask in an inclined position, until all the water has been driven off and the acid remains of a white or very pale-yellow colour. After removing the source of heat, add a little powdered permanganate until, on shaking, the liquid becomes green, showing that excess has been added. If a purple instead of a green colour appears, it shows that the whole of the water has not been driven off. When cool, 200 c.c. of water free from ammonia are added, care being taken to rinse round the neck of the flask, and thus wash in any acid which may be adhering there. 100 c.c. of sodium hydroxide solution are then added, and the mixture distilled with a Liebig's condenser. (The sodium hydroxide solution is prepared by dissolving 200 grms. of good caustic soda in 1250 c.c. of distilled water, adding 2 grms. potassium permanganate, and boiling down until the volume is rather less than 1000 c.c., making up to 1000 c.c. when cold.) The distillate is collected in a flask containing 50 c.c. of water free from ammonia, and 1 c.c. of dilute pure hydrochloric acid, and during the distillation of the first 50 c.c. the delivery tube of the condenser is made to dip into this acid liquid, whilst during the remainder of the distillation the flask is lowered so that the delivery tube is just above the liquid. The distillation is carried on until the whole of the ammonia has passed over, and the contents of the receiver are then 'Nesslerised' in the ordinary way. The most scrupulous care must be exercised to prevent access of ammonia from the air and reagents; a blank experiment should also be made for control.

Determination of dissolved oxygen. Much importance is, with very little reason, attributed by some analysts to this determination; it can, moreover, be rarely applied, as the samples must be collected with special precautions if the results are to have any value at all. The various processes in use have been examined by Kisch (Chem. Soc. Abstr. 1892, 98). *Reichardt's* method (Zeitsch. anal. Chem. 1872, 11, 271), as modified by Preusse and Tiemann (Ber. 1879, 12, 1768; Tiemann-Gärtner's Untersuch. d. Wassers, 278), consists in boiling a measured volume of water, and collecting the gases over a hot solution of caustic potash, the oxygen being then estimated either by explosion with hydrogen, or by absorption with potassium pyrogallate. In *Mohr's* method (Mohr's Titrirmethoden) the sample is mixed with an acid solution of ferrous sulphate of known strength, then with caustic soda to throw down ferrous hydroxide, and after remaining for a few hours (air, of course, being rigidly excluded), the precipitate is redissolved in sulphuric acid, and the remaining ferrous sulphate titrated with permanganate. In the *Schützenberger-Risler* process (Bull. Soc. chim. 1873, [ii.] 19, 152; 20, 145; Tiemann-Gärtner's Untersuch. d. Wassers, 277, 288; Catherine Williams and Ramsay, Chem. Soc. Trans. 1886, 760; Bernthsen, Ber. 13, 2277; Roscoe and Lunt, Chem. Soc. Trans. 1889, 552; Dupré, Analyst, 1885, 10, 156) the water is allowed to act on a solution of sodium hydrindigotin disulphonate, which is thereby converted into the blue compound, a standard solution of sodium hydrosulphite being then run in until the liquid is again colourless. In *Winkler's* process (Ber. 21, 2843) the water is mixed with a solution of manganous chloride, and then with potassium iodide and caustic potash; the precipitated manganous hydroxide absorbs the oxygen, passing into a higher state of oxidation. On adding hydrochloric acid the higher oxide of manganese gives rise to the liberation of an equivalent quantity of iodine, the amount of which is determined by titration with sodium thiosulphate. According to Kisch (*l.c.*), the results by the Reichardt-Preusse-Tiemann method are decidedly lower than those obtained by the Winkler process, which is in harmony with the experience of the writer. The results by Mohr's and Schützenberger's methods accord very well with those by Winkler; but Winkler's appears, on the whole, to be the most trustworthy, and the easiest to carry out. A modification of Winkler's method has been made by Rideal and Stewart (Analyst, 1901, 26, 141), and a more recent one reducing it to a colorimetric process by Rideal and Burgess (*ibid.* 1909, 34, 193).

A full description and discussion of the several methods will be found in Sutton's Volumetric Analysis.

The determination of dissolved oxygen has, in recent years, been much practised in connection with the rate at which dissolved oxygen is absorbed by sewage and effluents from sewage works. This matter is of importance as affording a measure of the readiness with which such liquids will remove the dissolved oxygen from a stream into which they are discharged. For Scudder's method, *see* Fowler's Sewage Works Analyses, or Sutton's Volumetric Analysis.

Determination of carbon dioxide. (1) The *total carbonic acid* is determined by completely precipitating as calcium carbonate with an excess of calcium hydroxide (a sufficient quantity of calcium chloride being added to decompose alkaline carbonates), then filtering off the precipitate, and determining the carbon dioxide in it in the usual way (Fresenius, Quant. An.; Tiemann-Gärtner, Die Untersuch. d. Wassers, 213). If the water is saturated with carbon dioxide under pressure, the above method must be preceded by Rochleder's process for estimating the gas which escapes on reducing the pressure to that of the atmosphere.

(2) The *free and semi-combined carbon dioxide* is determined by Pettenkofer's method, in which the water is treated with an excess of standard calcium hydroxide solution, and, after the precipitate has separated in a *crystalline* form, the clear liquid is decanted off, and the excess of lime ascertained in an aliquot part by titration with standard dilute oxalic acid, using phenolphthalein as indicator. If the water contains alkaline carbonates, sufficient neutral calcium chloride solution must be added to decompose them, whilst if there is a considerable proportion of magnesia salts, some ammonium chloride must also be added.

If the carbonic acid thus determined is subtracted from the total obtained according to (1), then the difference represents the combined carbonic acid. To this combined carbonic acid there corresponds, of course, an equal quantity of semi-combined, so that only any excess over and above this can be regarded as free carbonic acid. It must, however, be pointed out that the determination of total carbonic acid generally yields results which are below the truth by 1–1·5 units in 100,000 parts, in consequence of the solubility of normal calcium carbonate itself (*v.* Walker and Kay, J. Soc. Chem. Ind. 1912, 31, 1013.)

Determination of sulphuretted hydrogen. Colorimetrically with a solution of sodium nitroprusside, using for comparison a standard solution of sulphuretted hydrogen. The latter is standardised by taking a measured volume and adding an excess of decinormal sodium arsenite; shake well, and then acidify with hydrochloric acid. After the arsenious sulphide has completely subsided, dilute to 300 c.c., and filter through dry paper. Take 100 c.c. of the filtrate, remove acidity by means of solid sodium carbonate, add a drop of starch solution, and then run in decinormal iodine until a blue colour is obtained. This method may, of course, also be employed for the determination of the sulphuretted hydrogen in the water itself if present in sufficient quantity.

In using the colorimetric method, 300 c.c. of the water are treated with 5 c.c. sodium carbonate and 3 c.c. sodium hydroxide; allow the precipitate to subside for 1–2 hours, then decant or filter. To 250 c.c. of the filtrate in a colourless cylinder add 1 c.c. of sodium nitroprusside solution (4 grms. per litre), and for comparison take 245 c.c. distilled water, to which add 2 c.c. sodium hydroxide and as much of the standard solution of sulphuretted hydrogen as is required to produce precisely the same tint as is obtained with the water above. In this manner 0·1 part H_2S per 100,000 can be determined (Tiemann-Gärtner, Untersuch. d. Wassers, 232).

Sulphuretted hydrogen may also be accurately determined by means of centinormal iodine solution. 10 c.c. or other suitable volume of the latter are placed in a 500 c.c. flask, and the water added until the colour completely disappears; 5 c.c. of starch solution are then added, and centinormal iodine is run in until a blue colour is obtained, pure distilled water being added up to the 500 c.c. mark from a burette. On subtracting the sum of the volumes of iodine, starch solution, and distilled water added from 500 c.c., the volume of water which reacted with the iodine solution employed is ascertained. A correction should be made for the volume of iodine solution required to produce a blue colour.

BACTERIOLOGY OF WATER.

The great progress which has been made within recent years in our knowledge of infectious diseases, and of the processes dependent on bacterial life, renders it imperative that the subject of water supply should be considered from a bacteriological, as well as a chemical, point of view.

It has long been recognised that in making determinations of organic matter, ammonia, nitrates, &c., with a view to ascertaining the fitness or otherwise of water for drinking purposes, the concomitants of the living poisons of zymotic disease and not the morbific matters themselves, which were still more or less hypothetical entities, were being tested for, and that it was necessary that the living poisons themselves must be explored by biological, and not by purely chemical, methods.

Liquid and solid media.

The classical investigations on bacteria by Pasteur, Tyndall, Lister, Nägeli, Cohn, Fitz, Schloesing, Muntz, and others prior to 1880 were practically all made with liquid culture media only. Such culture media labour under several serious disadvantages:—

(1) Facility with which they become contaminated with bacteria and other organisms from the air and other surroundings;

(2) The competition which arises between the different microbes present may lead to the entire suppression of some through the overwhelming multiplication of others;

(3) The great difficulty of obtaining pure cultivations of specific micro-organisms.

The introduction of solid culture media by Koch at the beginning of the eighties, in the last century, led to great developments in bacteriology. An immense variety of investigations were now rendered possible which had long been awaiting attack. These new methods of bacteriological study were at once applied to the identification of the specific micro-organisms of numerous diseases, and to the investigation of the bacteria present, in *air*, *water*, *soil*, and all our other surroundings.

By means of *gelatin-plate-culture* it became possible to ascertain the number and the nature of most bacteria present in any material. Thus n the case of water the number and nature of the bacteria present in any sample could be determined, and by this means it was possible to ascertain the effect of any treatment or process of purification on the bacteria present n water. Thus it was applied by the writer in 1885 to the study of the removal of bacteria from water by artificial and natural *filtration*, by *subsidence*, and by *precipitation*.

The results obtained in investigations of this kind led to a great modification of the opinions which had previously been entertained with regard to the value of these processes in removing the zymotic dangers of water. Thus it was found that bacteria could be almost wholly removed from water by the process of sand filtration which had a comparatively insignificant effect on the organic matter and other ingredients discoverable by chemical analysis.

Similarly these methods of bacteriological nvestigation enabled such processes of water purification to be readily controlled. Thus if the safety of a water-supply depends on the efficiency with which the removal of bacteria by filtration s carried out, it is obvious that this efficiency should be continually controlled by bacterio-ogical examination, so that any defect in the working of the filters may be at once detected and rectified. The systematic control of water-works by bacteriological examination is now being very widely carried on with great benefit to the communities concerned.

With the discovery of the specific bacteria of cholera, of typhoid fever, and of many other diseases, attempts were naturally made to find hese specific pathogenic bacteria in contaminated water-supplies. The chance of such discovery by the ordinary method of plate-cultivation s, of course, hopelessly remote, because a single pathogenic organism must almost inevitably be accompanied in water by a host of non-pathogenic individuals, and amongst these multitudes of harmless forms the few harmful ones will under ordinary circumstances be overlooked, whilst, in the small quantities of water operated on, the pathogenic forms may be absent, although present in a larger bulk.

To surmount these difficulties, the natural device was to provide conditions which would be favourable to the particular pathogenic form being sought for and less favourable or even antagonistic to the multitude of non-pathogenic orms with which it would be accompanied. We may call the provision of such conditions he method of *enrichment or preferential culture*.

Such a method of enrichment was very satisactorily applied by Koch to the discovery of the *holera-bacillus* in the water of the Elbe at Hamburg during the epidemic of 1892. If 90 c.c. of he water under examination be incubated for 8 hours at 37° with 10 c.c. of a solution conaining peptone 10 p.c., and sodium chloride 0 p.c., cholera bacilli will be found in the thin urface pellicle, and from this cultures are made.

Typhoid fever is, of water-borne diseases, he most important in Western Europe. An normous amount of labour and ingenuity have been devoted in recent years to the discovery of the bacillus of this disease in water. That the problem is a very difficult one may be gathered from the fact that until recently *its detection even in the discharges of typhoid patients was very frequently abortive.*

The special difficulty attending the discovery of the typhoid bacillus depends on the circumstance that even in the intestine of the typhoid patient it is enormously outnumbered by other bacteria, and especially by the *Bacillus coli communis*, which, discovered by Escherich in 1886, has in recent years achieved the very greatest celebrity in the bacterial world.

Practically all conditions which are favourable to the typhoid bacillus are equally or even still more favourable to the *B. coli*, and for a long time all methods of favouring the typhoid bacillus at the expense of the *B. coli* proved futile. Much interest was, therefore, excited when in 1903 Roth announced that the *B. coli* was more disadvantageously affected than the typhoid bacillus by solutions of caffeine.

Experiments made by Kloumann[1] in 1904, however, showed that the differential effect on the two bacilli was only very slightly in favour of the typhoid bacillus.

A method of testing for typhoid bacilli in water and other liquids was elaborated by Hoffmann and Ficker in 1904; it was also based on the inhibitory action of caffeine and of crystal-violet on the *B. coli*. The method will be best understood by the following description of the manner in which it was successfully employed by Jaksch and Rau (1904) to detect typhoid bacilli in the drinking water supplied to Prague:—

900 c.c. water from a service tap were added to the *Hoffmann and Ficker culture-medium*, consisting of 10 grms. nutrose, 5 grms. caffeine, and 0·01 grm. crystal-violet, in 100 c.c. water.

The mixture was then incubated at 37° for 13 hours, when it was to be presumed that any typhoid bacilli originally present would have extensively multiplied. Loopfuls of this large cultivation were then withdrawn and spread on the surface of *Drigalski and Conradi Plates* (agar, meat extract, peptone, nutrose, lactose, sodium chloride, crystal violet and litmus), which were then incubated at 37° for 24 hours. On these plates the *B. coli* colonies are red (acid litmus) and non-transparent, whilst those of the typhoid bacillus are blue with a violet tinge, transparent, resembling dewdrops, and smaller than the *B. coli* colonies. In the Prague experiment these plates gave only a few red colonies, the majority being blue and transparent. The latter were sub-cultured, and, according to Jaksch and Rau, gave results in the most varied tests (including agglutination, toxicity, and immunisation) which were identical with those obtained with the true typhoid bacillus.

Other solid media which have proved of great value in distinguishing between coli-like and typhoid-like colonies are Loeffler's malachite-green agar, and McConkey's bile-salt-neutral-red agar, both of which will be referred to later.

By far the most extensive, interesting, and systematic search which has ever been made for the typhoid bacillus in natural waters is

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[1] Kloumann, Centralbl. f. Bakteriologie, 1904, 36, 512.

that carried out by Houston in the waters of the three rivers—Thames, Lea, and New River—from which the greater part of the London water supply is obtained. As this investigation illustrates the most approved methods which are now available to the bacteriologist, it will be considered here in some detail.

Two hundred and ninety-four experiments in 8 series were made with 156 samples of raw river water (52 Thames, 52 Lea, and 52 New River) during the 12 months ended July 31, 1908. The total volume of water dealt with was 294 × 100 = 29,400 c.c. The total number of bacteria in this volume of water (as ascertained by gelatin-plate cultivation for 3 days at 20°–22°) was 135,687,500. The total number of colourless (or nearly colourless) colonies sub-cultured from the Drigalski or similar plates was 7329. These 7329 selected colonies form but a small fraction of the millions of bacteria which were excluded owing to the temperature of incubation, the composition of the media employed, and the fact of their appearing on the plate-cultures as coloured colonies.

The following tabular summary indicates the method adopted in this exhaustive investigation:—

Direct Plating on Solid Media.

- Series I. 100 c.c. of the sample of water were centrifuged and the resulting deposit spread over a number of plates consisting of *malachite-green* (1 *in* 5000), *saccharose, dulcite, salicin, neutral-red, bile-salt, peptone, lactose, agar*. The plates were incubated at 40°–42° for 24 hours, and the colourless colonies sub-cultured into special media, as described in the next table.
- Series II. Same as Series I, but the proportion of malachite-green was 1 in 10,000.
- Series III. Same as Series I, but the media used in the plates contained no malachite-green.
- Series IV. Same as Series I, but the proportion of malachite-green was 1 in 20,000, 1 in 40,000, and 1 in 80,000.

Primary Liquid Cultures followed by Plating on Solid Media.

- Series A. 100 c.c. of the sample of water were added to *bile-salt-glucose-peptone medium containing malachite-green* in proportion of 1 in 1000, 1 in 2000, 1 in 4000. This liquid was incubated at 40°–42° for 24 hours, and then plated on the same medium as was employed in Series I, 10 colourless colonies were in each case sub-cultured and tested as described.
- Series B. Same as Series A, but malachite-green in the liquid medium was in proportion of 1 in 8000, 1 in 16,000, 1 in 32,000. Subsequently plated on same medium as that used in Series II.
- Series C. Same as Series A, but the liquid culture medium consisted of meat-broth only without malachite-green or any other additions. Subsequently plated on same medium as that used in Series I.
- Series D. Same as Series C, but instead of cultivating 100 c.c. of water in one portion, 10 cultures of 10 c.c. each were made.

The following table shows the behaviour of 32 strains of the typhoid bacillus, on the one hand, and of the 7329 suspicious colonies isolated from the raw waters, on the other. *It will be seen that not one out of all these 7329 different microbes, although suspicious in certain features, gave reactions agreeing in their entirety with those of the typhoid bacillus.*

VERIFICATION TESTS FOR TYPHOID BACILLUS.

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Description of microbe.	Proskauer's and Capaldi's No. 2 medium[1] (with inner tube).	Lactose-saccharose-dulcite-salicin-medium (with inner tube).	Proskauer's and Capaldi's No. 1 medium[2] modified (with inner tube).	Glucose-neutral red broth cultures (with inner tube).	Peptone-water medium.	Gelatin sugar media:—galactose, glucose, lævulose, maltose, and mannite respectively.
RESULTS CHARACTERISTIC OF TYPHOID BACILLUS.						
32 strains of typhoid bacillus from a number of different laboratories.	Acid, no gas	No visible change. (No acid, no gas.)	No visible change. (No acid, no gas).	Purplish tint. (No gas, no fluorescence.)	No indole.	Acid, but no gas with all five sugars. No liquefaction.
RESULTS WHICH EXCLUDE, AS NOT TYPHOID BACILLUS, THE SUSPECTED MICROBES.						
7329 colourless (or nearly colourless) colonies, sub-cultured.	No acid, or acid and gas	Acid or gas-formation.	Acid or gas-formation, or decided growth.	Gas or fluorescence. (Absence of purplish tint.)	Indole.	Gas formation in one or all of the sugar media. (Liquefaction.)

From the very nature of this investigation—the search for a specific microbe in a natural water which at some period of its history is practically certain to have received this microbe in comparatively small numbers—it is impossible to make it really exhaustive. Houston has

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[1] Solution of peptone and mannite.

[2] Solution of asparagine, mannite, glucose, galactose, lævulose, maltose, magnesium sulphate, sodium chloride, calcium chloride, potassium hydrogen phosphate, and litmus.

however, amplified his previous investigation in a very suggestive manner. Realising that the objection might be raised that the method adopted may not be capable of detecting a very small number of typhoid bacilli in the presence of a very large number of other microbes, he devised a mode of procedure which enabled him to affirm that in each particular sample of water examined there were *not more* than a certain definite number of typhoid bacilli in a given volume. The method adopted was this:—

Each sample of raw river water was divided into two equal portions of 500 c.c. (A and B). The A sample was inoculated with a very small number of typhoid bacilli. The B sample was not so infected, and was, therefore, normal raw river water. The subsequent procedure was exactly the same in each case, both samples A and B being treated exactly alike. The 500 c.c. of water were centrifuged and the resulting deposit spread over 16 plates prepared with solid medium of the following composition:

Agar, 2 grms.; peptone, 2 grms.; bile-salt, 0·5 grm.; lactose, saccharose, adonite, raffinose, and salicin, each 0·2 grm., made up with water to 100 c.c. and tinted with 0·4 c.c. of a 1 p.c. solution of neutral red. In some of the experiments malachite-green was added to the above, in the proportion of either 1 to 10,000, or 1 to 5000 of the medium.

Of the 24 experiments, 14 were carried out with raw Lea, and 10 with raw Thames, water. These waters contained on an average 62,688 bacteria per 1 c.c. (gelatin at 20°–22°, 3 days' incubation). The worst sample contained 760,000 and the best sample 1200 bacteria per 1 c.c. Thus in the 12 litres (500 c.c. × 24) of raw water (B samples) examined for typhoid bacilli there were 752,256,000 bacteria present.

The total number of colonies selected for study was 5451 from the infected A samples, and the same number (5451) from the non-infected B samples. The average number of typhoid bacilli artificially added to the A samples was 2·242 per 1 c.c. or 1121 per 500 c.c. The average number of typhoid bacilli isolated from the A samples was 14·54 per 500 c.c. of sample. It may be argued fairly, therefore, that if only $\frac{1}{14\cdot54}$ of the above number of typhoid bacilli had been present in the infected sample this microbe would still have been detected by the method of investigation adopted; but $\frac{1}{14\cdot54} \times 2\cdot242 = 0\cdot154$ typhoid bacillus per 1 c.c., or 1 typhoid bacillus in 6·5 c.c. would have been detected.

From the uninfected B samples, out of the 5451 colonies selected for special study, *one, and only one, consisted of bacteria which resembled the typhoid bacillus very closely.*

It will be instructive to record the observations which were made on submitting this typhoid-like microbe (*Lee W.* 694 ? *B. typhosus, Houston*) to the several tests used in the diagnosis of typhoid bacilli.

Characterisation of typhoid-like bacillus from raw river water (Lea W. 694 ? B. typhosus, Houston).

Morphology. A motile multiflagellate bacillus. The rods seemed shorter than in most strains of *B. typhosus.*

Gelatin and agar slope-cultures. Possibly the growth was slightly less filmy in character than that of the true *B. typhosus.*

Glucose-bile-salt agar-slope (neutral red). The streak somewhat brighter and cleaner red than in most strains of *B. typhosus.*

Lactose-bile-salt agar-slope (neutral red). Colourless streak.

Potato. No visible growth (5 days at 37°).

Nitrate-broth. Reduces nitrates to nitrites.

Peptone-water at 55°F. No visible growth after 5 days; on transferring tube to incubator at 37°C. growth occurred within 24 hours.

Indole test. No indole formation (5 days at 37°).

Liquid peptone (1 p.c.) *media* containing separately 1 p.c. of the substances stated and tinted with litmus. Sorbite and inosite are only used in 0·2 p.c. solution. Acid but no gas in sorbite, mannite, glucose, lævulose, galactose, and maltose respectively (2 days at 37°). No change in inulin, inosite, saccharose, salicin, adonite, lactose, dulcite, and raffinose respectively (5 days at 37°).

Gelatin glucose medium tinted with litmus. Acid but no gas formation.

Voges and Proskauer's reaction. Negative result, 5 days.

Gelatin. No liquefaction after one month at 20°.

Litmus milk. Slight acid but no coagulation (5 days at 37°).

Glucose-neutral-red-broth cultures. No gas, no fluorescence characteristic purplish tint.

Lactose-saccharose-dulcite-salicin-peptone medium tinted with litmus. No change (2 days at 37°).

Proskauer and Capaldi's Medium No. 1 (*modified*). No change (2 days at 37°).

Proskauer and Capaldi's Medium No. 2. Acid but no gas.

Agglutination experiments and tests for pathogenicity.

Anti-typhoid serum. Microscopically, 1 : 200 almost instantaneous clumping, 1 : 800 very fair clumping, 1 : 2000 little or none. *B. typhosus* tested with the same serum gave very similar results but appeared to be clumped slightly more rapidly and in slightly higher dilutions. The difference, however, if any, was not well marked.

Serum of an animal immunised with the suspected microbe (*Lea W.* 694 ? *B. typhosus, Houston*). Microscopically, 1 : 200 very rapid and satisfactory clumping; 1 : 2000 good, but not quite complete clumping within half an hour.

B. typhosus tested with the same serum gave very similar results, but was perhaps clumped a little more slowly and in slightly lower dilutions. The difference, however, if any, was not well marked. Microscopically, the titre limit was about 1 : 8000 (18 hours) and was practically the same for both microbes.

Pathogenicity. 2 c.c. of a broth-culture injected subcutaneously into a guinea-pig produced a swelling and illness with recovery. A guinea-pig intraperitoneally inoculated with 5 c.c. of a broth-culture died in less than 24 hours.

On the results of this laborious investigation, which had extended over more than two years, and which had been conducted with the most meticulous care and regardless of time and money, Dr. Houston very cautiously remarks: '*If this microbe had been isolated from a case of typhoid fever* (*or from a suspected case*) *I do not think any serious hesitation would have been felt in describing it as B. typhosus.*'

It would be impossible to produce more eloquent testimony than the above as to the enormous and almost prohibitive trouble which a systematic and conscientious search for the typhoid bacillus in a natural water entails.

Comparative unimportance of searching for the typhoid bacillus in water. The almost hopeless nature of the search for the typhoid bacillus in natural waters is of the less importance as the anxiety to detect this microbe in water is, for the most part, based upon an entire misconception of the objects of water examination. The object of a water examination is, in general, not to determine whether the particular sample of water contains typhoid bacilli and is, therefore, capable of carrying typhoid to the consumer, but to discover whether the water is likely *at any time* to contain such infective material.

Now any water which receives sewage matters must be regarded as a *possible* carrier of typhoid infection, for at any time these sewage matters may be derived from persons suffering from typhoid. Thus any sewage-contaminated water is a potential carrier of typhoid unless it has been subjected to conditions which would ensure the removal of the possibly present typhoid bacillus. Thus the all-important thing is to ascertain whether a given water has been contaminated with sewage, in what proportion such contamination has taken place, and whether the water since such contamination has been submitted to conditions which would remove or destroy typhoid bacilli should they have gained access with the sewage matters.

Firstly, as regards the detection of sewage contamination. Excremental contamination, if sufficient in amount, can be revealed with more or less certainty by chemical analysis, which can indeed even distinguish between whether such pollution is recent or remote in point of time, but in order to ascertain the fate of bacteria gaining access to water recourse must be had to biological methods. If there were bacteria absolutely characteristic of sewage, the determination of their presence would be sufficient to prove the danger of a water. Unfortunately we do not know of any bacteria which satisfy the condition of being *absolutely* characteristic of sewage, so we must be satisfied with a second best qualification for diagnostic purposes by those which are *very* characteristic of sewage.

The microbe which is most characteristic of the intestinal discharges of man and the higher animals is, as its name implies, the *B. coli communis*, and a great amount of time and ingenuity has been devoted to its accurate and expeditious discovery in water and other materials.

In identifying a particular organism, whether plant or animal, we depend on recognising in the individual a certain group of specific characters which are more or less arbitrary. The botanist at first tried to classify and distinguish bacteria by external appearances alone; he measured the length and breadth of these minute organisms; he counted the number of flagella with which some of them are provided; he was very careful to observe whether they were square or round at the ends, and so forth.

These morphological characters have, however, long been recognised as inadequate for purposes of identification, since organisms exhibiting the closest morphological similarity have been found to differ enormously in other respects.

After the introduction of Koch's methods much attention was directed to the macroscopic appearances to which the organisms give rise when grown on a variety of solid media, by which means microscopically similar bacteria can often be differentiated.

Some 20 years ago the writer commenced distinguishing bacteria, which were similar in form and in cultural appearances, by differences in the chemical changes which they could bring about in certain media. Thus he found that the capacity to reduce nitrates to nitrites was in some cases a valuable means of distinguishing between otherwise similar bacteria. This reduction of nitrates has been extensively used for diagnostic purposes, more especially by American bacteriologists. Somewhat later he devoted much attention to the fermentaion of carbohydrates, polyhydric alcohols, and hydroxyacids, by means of pure cultivations of micro-organisms, and showed how capricious is the power possessed by different bacteria in this respect. Thus perhaps one microbe will ferment glucose, mannite, and glycerol, but not dulcite or glyceric acid, another will ferment glucose, mannite and dulcite, &c.

This mode of differentiating between otherwise very similar forms of bacteria has been greatly extended within recent years. In the following table the classification of the Typhoid-coli group of bacteria into seven subgroups has been attempted :—

TYPHOID-COLI GROUP.

Sub-groups	Glucose	Acid gas	Lactose	Acid gas	Dulcite	Acid gas	Saccharose	Acid gas
I.								
B. *Typhosus* . . .	+	−	−	−	−	−	−	−
B. dysenteriæ . . .	+	−	−	−	−	−	−	−
B. fæcalisalcaligenes . .	−	−	−	−	−	−	−	−
II.								
B. enteritidis (Gaertner) .	+	+	−	−	+	+	−	−
B. paratyph . . .	+	+	−	−	+	+	−	−
B. paracoli	+	+	−	−	+	+	−	−
III.								
Bacillus from urine . .	+	+	−	−	−	−	+	+
IV.								
B. acidi lactici (Hueppe) .	+	+	+	+	−	−	−	−
V.								
B. coli (Escherich) . .	+	+	+	+	+	+	−	−
VI.								
B. pneumoniæ (Friedländer) .	+	+	+	+	+	+	+	+
VII.								
B. capsulatus (Pfeiffer) .	+	+	+	+	−	−	+	+
B. lactis aërogenes (Escherich)	+	+	+	+	−	−	+	+
B. cloacæ (Jordan) . .	+	+	+	+	−	−	+	+

There are, however, many bacteria which more or less simulate the characters of the typhoid bacillus on the one hand, and of the *B. coli* on the other; such forms exhibit almost every degree of approximation to one or other of these two types, from which they can only be distinguished by applying a number of tests. Such forms are designated as *atypical*, and what their relationship to the typical typhoid and coli bacteria may be is a matter of uncertainty. Possibly in some cases they may have been typical forms originally, but under the particular conditions to which they have been submitted they have lost some of their characters. Thus it is often found that the *B. coli*, on prolonged artificial culture, may lose either or both its indole-producing and milk-curdling properties

It is obvious that by increasing the number of biochemical tests many further variations of a given type of organism may be discovered, and, for the purpose of more precisely defining a particular microbe, bacteriologists have introduced biochemical tests involving the use of a variety of organic compounds—more especially carbohydrates, polyhydric alcohols, and glucosides. These tests generally consist in ascertaining whether an organism under investigation gives rise to acid or gas, or both, or neither, in a suitable nutritive medium containing one of these substances. The following list of substances employed in this manner will give some idea of the degree to which these biochemical tests have been complicated in recent years: adonite, asparagine, dextrin, dulcite, erythrite, galactose, glucose, glycerol, glycol, *iso*dulcite, lactose, lævulose, maltose, mannite, mannose, nutrose, raffinose, sucrose, salicin, sorbite, and starch. The above list by no means exhausts the number of organic substances which are acted on by bacteria, and by means of which, therefore, differences can be established.

Although such tests are extremely useful for the more precise definition of particular micro-organisms, they must be employed with discrimination, for as the writer long ago pointed out, these fermentations, as well as other characters of bacteria, are liable to be lost through conditions of environment, and he has also shown how in some cases they may be restored by resorting to particular methods of culture and training.

It is obvious that it would be impracticable to resort to such numerous tests in the ordinary bacteriological examination of water in which we are concerned with the detection of sewage or excremental contamination, unless some very great advantage should result from such multiplication of tests, and this is not the case at present.

Quantitative determination of B. coli in water. If we regard the *B. coli* provisionally as the best indicator of contamination with the living bacteria of animal refuse, we shall obviously view its presence with the more suspicion the larger the numbers in which it is discovered in a given volume of water.

The numerous methods which have from time to time been devised for detecting *B. coli* will be passed over, and only the one which in this country at any rate has superseded all others will be described.

An important departure in practical bacteriology was the introduction by McConkey and Hill ('Bile-salt broth. A simple test for fæcal contamination.' Thompson-Yates Laboratories Report, 1901, 4, [i.] 151) of a medium for the preferential culture of the *B. coli* and allied microbes from mixtures of micro-organisms. The essential ingredients of this medium are sodium taurocholate (bile-salt), 5 grms., glucose, 5 grms., peptone, 20 grms., water (tinted with litmus), 1000 c.c. Incubated in this liquid at 37°–42° bacteria of the *B. coli* group give acid and gas in 48 hours. Some bacteriologists use lactose instead of glucose, thus restricting the gas production to *B. coli* and its still closer allies. With this liquid medium in Durham fermentation-tubes cultivations of the water are made in the following quantities: 100, 10, 1, 0·1, 0·01, 0·001, 0·0001, 0·00001 c.c. The concentration of the medium should in all cases be approximately the same as that given above. In order, therefore, that the volumes of liquid incubated may not be inconveniently large, the 10 and 100 c.c. of water are introduced into correspondingly stronger McConkey media.

A positive reaction, *i.e.* the production of acid and gas, in any of these culture-tubes signifies that *at least one* coli-like microbe must have been introduced with the portion of water added. Thus, if acid and gas had been obtained, in a particular case, with all the tubes from 100 to 0·1 c.c., this would mean the '*presumptive*' presence of at least one *B. coli* in 0·1 c.c., and its absence in 0·01 c.c. and smaller volumes of water.[1]

In order to ascertain whether the 'presumptive' *B. coli* is typical or not, the tube containing the smallest portion of water which has given rise to acid and gas in the McConkey medium is plated on a solid medium of the following composition: Agar 20 grms., peptone 20 grms., sodium taurocholate (bile-salt) 5 grms., lactose 10 grms., neutral red (1 p.c. solution), 4 c.c., made up to 1000 c.c. with water. After 12 hours' incubation at 37°, the colonies will be distinctly visible, and those which are most likely to be *B. coli* will have a strong red colour owing to the acid produced by this microbe in the medium. Five of the most typical red colonies are separately inoculated into 5 glucose-litmus broth tubes, which are then incubated at 37°. Any of these 5 tubes which develop acid and gas are then each further inoculated into tubes of the following media which are then incubated at 37°:—

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[1] There is one element of uncertainty connected with such tests made in liquid media which appears to be tacitly ignored by all bacteriologists who make use of them, and that is that the particular microbe sought for may in the process of cultivation in the liquid medium become hopelessly outnumbered or even suppressed by the much more abundant proliferation of some other microbe or microbes present in the mixture.

Thus the McConkey medium may be taken as specially favourable for the proliferation of bacteria of the *B. coli* type, but the water-bacteriologist is in general restricting his search to those bacteria which are sufficiently like typical *B. coli* as to produce acid *and* gas in the medium. Is it not possible that the bacteria capable of producing both acid and gas may be so greatly outnumbered by microbes not giving this reaction that the more typical *B. coli* forms may be so much kept in abeyance that no acid and gas reaction is obtained? Under these circumstances he would obviously draw the conclusion, and quite erroneously, that acid and gas producing microbes (and, therefore, *B. coli* amongst them) were absent. This is a matter which requires much further investigation before the conclusions as to *absence* of *B. coli* generally drawn can be justified.

(*a*) Neutral red broth to be examined for fluorescence.

(*b*) Litmus lactose-broth to be examined for *acid and gas.*

(*c*) Ordinary broth to be examined for *indole.*

(*d*) Litmus-milk to be examined for *acid and coagulation.*

(*e*) Gelatin to be examined for *non-liquefaction.*

The above glucose-tubes from which these inoculations have been made are also microscopically examined to see whether the microbe possesses the characteristic form and motility of the *B. coli.*

A microbe fulfilling these conditions has been designated by Houston as '*Flaginac*' *B. coli*, from Fl=fluorescence in neutral-red broth, ag=acid and gas in lactose, ín=indole in peptone broth, ac=acid and coagulation in litmus-milk.

The typical *B. coli* from human fæces gives these reactions, but, of course, it is possible to further differentiate between coli-bacteria by additional tests, such as fermentation of sucrose, dulcite, mannite, &c., but at present there would not appear to be any advantage in such multiplication of tests in the ordinary examination of water.

The following table summarises an interesting investigation made by Houston on the proportion of 'Flaginac' *B. coli* found amongst the coli-like microbes obtained from different sources:—

FLAGINAC B. COLI.

Source	Number of specimens of *B. coli* or coli-like microbes on which percentage is based	P.c. of flaginac *B. coli*
Milk . . .	343	61
Human fæces . .	101	85
Sewage . . .	several hundreds	65–85
Oysters . . .	464	43
Estuarial waters .	183	66
Water-cress . .	81	40
Washings of cress .	52	52
Water in which cress was grown . .	42	76
London filtered water	232	31

In the following table are recorded the results of some very suggestive pioneering experiments made by McConkey (1905), undertaken with the object of ascertaining whether there is any marked difference in the types of *B. coli* found in the excreta of man and some of the common domestic animals respectively. Should it be possible to establish such a difference, an important means of distinguishing between human and animal excrementitious contamination of water would be obtained.

B. COLI FROM HUMAN AND ANIMAL EXCRETA (MCCONKEY).

Group	Fermentation of		Number of lactose-fermenting Coli-form microbes isolated and experimented with			Results in percentages		
	Saccharose	Dulcite	Human	Animal[1]	Total	Human	Animal	Average
I.	—	—	83	37	120	34	15	25
II.	—	+	93	85	178	38	36	37
III.	+	+	36	74	110	15	31	23
IV.	+	—	29	43	72	12	18	15
			241	239	480	100	100	100

[1] Twenty-five samples of animal excreta, of which 5 were from horses, 6 from cows, 3 from rabbits, 1 from a monkey, and 14 from a cat.

Source	Approximate number per 1 gram. of excreta		
	B. coli	*Streptococci*	*B. enteritidis sporogenes* spores
Horse No. 1 . . .	Over 1 million	$\frac{1}{10}$ to 1 million	10 to 100
Horse No. 2 . . .	$\frac{1}{10}$ to 1 million	Over 1 million	100 to 1000
Horse No. 3 . . .	1000 to 10,000	Over 1 million	100 to 1000
Cow No. 1 . . .	$\frac{1}{10}$ to 1 million	10,000 to 100,000	100 to 1000
Cow No. 2 . . .	10,000 to 100,000	$\frac{1}{10}$ to 1 million	10 to 100
Cow No. 3 . . .	1 to 10 millions	Over 10 millions	10 to 100
Cow No. 4 . . .	1 to 10 millions	$\frac{1}{10}$ to 1 million	100 to 1000
Pig No. 1 . . .	Over 100 millions	Absent	$\frac{1}{10}$ to 1 million
Pig No. 2 . . .	10 to 100 millions	Absent	10,000 to 100,000
Pig No. 3 . . .	70 millions	Absent	1000 to 10,000
Sheep No. 1 . . .	10 to 100 millions	1 to 10 millions	10 to 100
Sheep No. 2 . . .	10 to 100 millions	10 to 100 millions	10 to 100

Such an investigation would have to be enormously extended before results capable of being used for diagnostic purposes could be obtained.

An attack on the same important problem was also made by Dr. Wm. G. Savage (1904–5) in an extremely laborious investigation, which he has summarised in the foregoing table.

The absence of streptococci in the fæces of the pig is extremely remarkable.

It is convenient to classify waters tentatively according to the results of the examination for *B. coli*, thus :—

Classification of Water by B. Coli Test.

(1 c.c. of sewage is assumed to contain 100,000 *B. coli*.)

Class	Volume of water examined	*B. coli* per 1 c.c.	Pollution in sewage
	c.c.		per cent.
I .	— in 100	0	—
II .	+ in 100	0·01	0·00001
III .	+ in 10	0·1	0·0001
IV .	+ in 1	1	0·001
V .	+ in 0·1	10	0·01
VI .	+ in 0·01	100	0·1
VII .	+ in 0·001	1000	1
VIII .	+ in 0·0001	10,000	10
IX .	+ in 0·00001	100,000	100 (pure sewage)

This classification must not, however, be interpreted too rigidly, as it is based on the assumption that *B. coli* is always derived from fæces and that this microbe is incapable of multiplication under any circumstances after incorporation in what is known as 'sewage.'

In the two following tables are recorded the results of the ordinary bacteriological examination of a number of typical waters. The tables sufficiently explain themselves.

Storage of water. In 1886 (Water Purification, its Biological and Chemical Basis, Trans. Inst. Civil Engineers, 1886) the writer pointed out the great importance from a theoretical point of view of storage for the purification of surface waters. In 1892, again, he investigated the influence of storage on the bacteriological purity of the river waters abstracted for the supply of London, and showed that there is a most striking reduction in the number of suspended micro-organisms during storage in large reservoirs.[1]

The great importance of storage from the hygienic point of view was further manifest from the experiments made on the fate of pathogenic bacteria introduced into natural waters, and which showed that the duration of life of these bacteria under such conditions is generally very short.

In 1891–4 the writer had the opportunity of greatly extending his observations on this subject, as he was requested by a Committee of the Royal Society to make, in conjunction with the late Professor Marshall Ward, F.R.S., a special inquiry into the vitality of pathogenic bacteria in potable waters (*see* Proc. Roy. Soc.). The experiments were restricted to the study of the behaviour of the anthrax bacillus (and its spores), the typhoid bacillus, and the *B. coli communis*, and the potable waters employed were those of the Thames, Loch Katrine, and deep-well water from the chalk, these being fairly typical of the different kinds of water used for drinking purposes in this country. Experiments were made with these waters in their natural, and also in a sterilised, condition.

Birmingham Water Supply. (P. F. Frankland.)

Averages for 1910.

	Number of bacteria				*Bacillus coli* (typical)						
	Gelatin at 20° C.		Carbolic gelatin at 20° C.	Tauro-cholate agar at 37° C.	100 c.c. −	100 c.c. +	10 c.c. +	1·0 c.c. +	0·1 c.c. +	0·01 c.c. +	0·001 c.c. +
	2 days	7 days	7 days	4 days							
					p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Whitacre [1]—											
Unfiltered .	3300	—	167	1232	—	—	—	8·3	16·7	58·3	16·7
Filtered .	12	87	0	5	75·0	25·0	—	—	—	—	—
Frankley [2]—											
Inlet . .	37	237	0·7	13	18·2	45·5	36·4	—	—	—	—
Reservoir .	54	258	1·6	40	41·7	33·3	25·0	—	—	—	—
Filtered .	5	38	0	3	91·7	8·3	—	—	—	—	—
City mains .	19	59	0·03	5·5	78·4	16·2	5·4	—	—	—	—

[1] Surface water from more or less cultivated land.

[2] Moorland water from Elan Valley, Wales.

The results obtained may be summarised as follows :—

(1) Unsterilised water infected with anthrax bacilli containing spores was still virulent after being kept for 7 months.

(2) Anthrax bacilli taken directly from an animal dead of anthrax, and, therefore, free from spores, died rapidly (mostly in 5 days) when introduced into unsterilised water kept at low temperatures (5° and 13° in these experiments), but when introduced into the same waters and kept at 19°, the bacilli formed spores, and the latter were still present in enormous numbers

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[1] Appendices to Minutes of Evidence, Roy. Commission on Metropolitan Water Supply, 1893, 469—475. See also "Micro-organisms in Water," P. Frankland and G. C. Frankland, London, 1894, pp. 99, 126, 131—142, 184.

LONDON WATER SUPPLY. (Houston.)

Averages for 1908–9 *and* 1909–10.

	No. of bacteria gelatin at 20°–22° C. 3 days	*Bacillus coli* (typical)									
		100 c.c. −	100 c.c. +	10 c.c. +	1·0 c.c. +	0·1 c.c. +	0·01 c.c. +	0·001 c.c. +	0·0001 c.c. +	0·00001 c.c. +	0·000001 c.c. +
Raw River Waters—											
		p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Thames at Hampton, 1908–9 . . .	2558	—	2·1	10·3	40·1	36·6	10·4	0·4	—	—	—
Thames at Hampton, 1909–10 . . .	5268	0·5	0·5	6·3	26·9	52·9	12·8	—	—	—	—
Lea at Ponder's End, 1908–9 . . .	8794	—	0·8	5·2	34·9	38·8	15·5	3·9	0·8	—	—
Lea at Ponder's End, 1909–10 . . .	37,071	—	0·5	6·3	31·4	39·7	13·2	7·3	0·5	0·5	0·5
New River at Hornsey, 1908–9 . . .	1118	2·1	9·1	40·9	38·8	8·2	0·8	—	—	—	—
New River at Hornsey, 1909–10 . . .	2801	0·9	8·3	41·7	36·8	9·8	2·4	—	—	—	—
Filtered Waters—											
Thames, 1908–9 . .	89	83·4	11·8	3·9	0·7	0·06	—	—	—	—	—
,, 1909–10 . .	55	81·8	14·6	2·7	0·7	0·09	0·02	—	—	—	—
Lea, 1908–9 . . .	163	85·1	10·1	4·1	0·7	—	—	—	—	—	—
,, 1909–10 . .	237	88·1	8·9	2·3	0·6	—	—	—	—	—	—
New River, 1908–9 .	7	88·3	9·4	2·0	0·07	0·07	—	—	—	—	—
,, ,, 1909–10 .	16	82·6	14·1	2·9	0·3	—	—	—	—	—	—
Deep Wells—											
Kent, 1908–9 . .	6	92·3	4·7	1·2	1·7	—	—	—	—	—	—
,, 1909–10 . .	8	96·2	3·3	0·4	—	—	—	—	—	—	—
Lea Valley, 1908–9 .	19	79·1	13·6	2·7	4·5	—	—	—	—	—	—
,, ,, 1909–10 .	16	89·0	8·8	2·1	—	—	—	—	—	—	—

even 42 days later, and doubtless for a much longer period still. This remarkable difference in behaviour is accounted for by the fact, previously discovered by Koch, that anthrax bacilli do not form spores below 16°.

The following results were obtained by introducing typhoid bacilli from one and the same cultivation and in the same numbers into each of the waters at one and the same time:—

Unsterilised water	Life of typhoid bacilli
Thames water (Oct. 19, 1893) 9°–12°	Between 9 and 13 days
Loch Katrine water (Oct. 19, 1893) 9°–12°	,, 19 ,, 33 ,,
Deep well water (Oct. 19, 1893) 9°–12°	,, 33 ,, 39 ,,
In two other separate experiments with unsterilised Thames water (May 11, 1893)	,, 25 ,, 34 ,,
and (Jan. 16, 1894) . .	,, 20 ,, 27 ,,

In all these experiments only 1 c.c. of water was examined for typhoid bacilli, and the method of search, the best known at the time, was that due to Parietti, in which the water is cultivated in a phenol-broth medium at 37°, which on becoming turbid is submitted to plate cultivation, the colonies obtained being then examined in detail for identification

It is particularly interesting to compare with the above results those obtained by Houston in a perfectly similar inquiry and making use of all the most modern developments of bacteriological technique. Dr. Houston made 18 experiments on raw Thames, Lea, and New River waters, infecting them with typhoid bacilli (the number added being in all but three experiments very large, *see* table below). The presence of the bacillus was tested for at weekly intervals in 1 c.c. by means of a medium containing *Agar-bile-salt-dulcite-lactose-saccharose-salicin-peptone-neutral-red-malachite-green*, and which is specially designed to favour the growth of this microbe whilst repressing that of most others. The results may be summarised in the following statement:—

In 3 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 1 week.

In 10 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 3 weeks.

In 16 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 4 weeks.

In 18 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 5 weeks.

Thus, notwithstanding the great advances made in the technique of testing for the typhoid bacillus, the results obtained by Houston are essentially similar to those obtained by the writer 15 years previously. Houston has, however, extended the investigation in an interesting manner by ascertaining the length of time required before even 100 c.c. of the infected water gave a negative result on being tested by the most modern methods for the presence of the typhoid bacillus. The whole of Houston's investigation (both for 1 c.c. and for 100 c.c. of water tested) is instructively summarised in the table below.

Description of water	Initial No. of typhoid bacilli in 1 c.c. of infected water	Number of typhoid bacilli in 1 c.c. of infected water after						Number of weeks required for destruction of typhoid bacillus in 100 c.c. of infected water
		1 week		2 weeks	3 weeks	4 weeks	5 weeks	
			(p.c. reduction)					
Thames (I) .	40	0	100	—	—	—	—	5
Lea (I) . .	40	0	100	—	—	—	—	5
New River (I) .	40	0	100	—	—	—	—	6
Thames (II) .	170,000	9	99·9	2	0	—	—	6
Lea (II) . .	170,000	53	99·9	2	0	—	—	5
New River (II) .	170,000	40	99·9	2	0	—	—	6
Thames (III) .	470,000	480	99·9	31	5	0	—	8
Lea (III) . .	470,000	850	99·8	11	7	2	0	7
New River (III)	470,000	1430	99·7	14	7	0	—	7
Thames (IV) .	8,000,000	3000	99·9	30	4	0	—	8
Lea (IV) . .	8,000,000	2900	99·9	29	5	0	—	8
New River (IV)	8,000,000	400	99·9	22	2	0	—	9
Thames (V) .	525,000	12	99·9	1	0	—	—	8
Lea (V) . .	525,000	32	99·9	2	0	—	—	7
New River (V) .	525,000	29	99·9	3	0	—	—	5
Thames (VI) .	475,000	210	99·9	12	2	1	0	9
Lea (VI) . .	475,000	80	99·9	11	2	0	—	8
New River (VI)	475,000	30	99·9	3	0	—	—	7

This table shows, on the one hand, that whilst in each case nearly all the typhoid bacilli are destroyed by a single week's residence in these raw river waters a few individuals persist for a much longer period of time. This illustrates in a very interesting and instructive manner a principle emphasised by the writer some 16 years before, 'that one of the factors determining the longevity of pathogenic bacteria placed in water, or for the matter of that placed in any unfavourable surroundings, is the absolute number in which they are present. In other words, amongst, for instance, 1000 bacteria taken from a given source there may be *some individuals* which will resist a particular adverse influence, whilst amongst 10 bacteria taken from the same source there may be *none* capable of resisting the adverse influence in question' (P. F. Frankland, Proc. Roy. Soc. 1894, 56, 486).

Before leaving the subject of the behaviour of the typhoid bacillus in water, mention must be made of some extremely interesting and ingenious experiments by the American bacteriologists, Jordan, Russel, and Zeit, in 1903. These investigators endeavoured to imitate natural conditions more closely than has been done in any other experiments by placing the typhoid-infected waters in permeable sacs made of celloidin and parchment, and then by submerging these in river, canal, or lake water, their contents were exposed to the influence of the dialysable substances present in the water under natural conditions.

Zeit experimented with Lake Michigan water and Chicago river water, the natural bacterial content of which varies between 68 and 2000 microbes per 1 c.c. in the case of the Lake, and between 80,000 and 1,500,000 microbes per 1 c.c. in that of the river water. Parallel experiments were made with infected water placed in ordinary bottles and in permeable sacs respectively. The typhoid bacilli introduced varied between 500 and 2,000,000 per 1 c.c. The destruction of the typhoid bacillus was taken as complete when negative results were obtained on cultivating 5 c.c. of the water, the death of the typhoid bacillus being generally confirmed by the subsequent cultivation, a few days later, of much larger volumes, sometimes as much as 800 c.c., of the water. Nine experiments were made with the Michigan Lake water, *the typhoid bacillus being never found after the eighth day.* Five experiments were made with the Chicago River water, *the typhoid bacillus being never found after the third day.*

Jordan experimented with the water of the Chicago Drainage Canal, which usually contains from 100,000 to 400,000 bacteria per 1 c.c. This water was infected with from 180 to 857,000 typhoid bacilli per 1 c.c. In these experiments, however, the maximum volume submitted to cultivation appears to have been only 1 c.c., and from negative results with even smaller volumes the death of the typhoid bacillus seems to have been concluded. Twenty-eight experiments were made in permeable sacs submerged in the canal, *the typhoid bacillus being never detected after the second day, excepting in one experiment in which it was still found on the tenth day.*

Russel's experiments were made with the Illinois River water, which contains from 1800 to 4000 bacteria per 1 c.c. This water was infected with 540 to 20,000 typhoid bacilli per 1 c.c. However, in these experiments, again, 1 c.c. appears to have been the maximum volume of water cultivated for the detection of the typhoid bacillus. Fourteen experiments were made in permeable sacs submerged in the Illinois River, *the typhoid bacillus being never found after the third day, excepting in one case in which it was detected on the ninth day.*

More recently, again, Houston has taken typhoid bacilli not from cultivations but from the human subject and introduced them into raw Thames water. He found that such bacilli perished very rapidly—much more quickly in fact than had been his experience with cultivated strains of the microbe.

The uncultivated typhoid bacteria were obtained from the urine of a 'typhoid carrier,' and on Aug. 9, 1910, the centrifugalised deposit (3·5 c.c.) from 389 c.c. of urine was added to 5000 c.c. of raw Thames water; the number of typhoid baccilli was determined as follows:—

At time of mixture, 770,000 typhoid bacilli per 1 c.c. of river water.

After 1 week, 4 typhoid bacilli per 1 c.c. of river water.

After 2 weeks, 0 typhoid bacilli in 100 c.c.

On the 24th day from the commencement of the experiment half-a-pint (about 284 c.c.) of the infected water was drunk, this quantity of water having *originally* contained 218,680,000 typhoid bacilli. Similar amounts were drunk with impunity on the 25th, 26th, 27th, and 28th days after the beginning of the experiment.

On Aug. 19, 1910, the experiment was repeated with a fresh sample of urine, the number of typhoid bacilli per 1 c.c. of river-water being 1650. A week later no typhoid bacilli could be found, and on the 23rd, 24th, 25th, 26th, and 27th day from the beginning half-a-pint of the infected water was drunk each day without any ill-effect (Sixth Research Report, Metrop. Water Board, Nov. 1910, p. 7).

If this drinking part of the experiment is to prove anything it would be necessary for Dr. Houston to follow it up by drinking a similar number of *fresh* typhoid bacilli from the same patient and contracting the disease, for without this last act we have no certainty that Dr. Houston is susceptible to this malady, and, therefore, a fit *corpus vile* on which to make this crucial test.

Vitality of the Spirillum of Asiatic cholera in potable water. Experiments were made by Houston with the cholera spirillum on exactly the same lines as those which he had previously adopted in the case of the typhoid bacillus in raw Thames, Lea, and New River water. The principal conclusions arrived at may be summarised as follows (4th Report on Research Work, Metrop. Water Board, June. 1909):—

'(1) Cholera vibrios die very rapidly in *raw* Thames, Lea, and New River water as the result of storage in the laboratory. At least 99·9 p.c. perished within one week, and in none of the experiments could any cholera vibrios (recognisable as such) be found even in 100 c.c. of water 3 weeks after its infection. In more than half the experiments the results were negative by the second week.

'(2) The isolation of cholera vibrios from *artificially* infected *raw* river water presents no insuperable difficulties even when the number artificially added is very small, both actually and relatively to the bacteria nominally present in the river water.

'(3) On the other hand, microbes liable (after careful study) to be mistaken for true cholera vibrios were not found in comparable, but non-infected, river water samples examined under precisely similar conditions.'

Thus the cholera vibrios are much more perishable in these raw river waters than are the typhoid bacilli under similar conditions.

The comparatively short duration of life of pathogenic bacteria when introduced into natural waters and more especially into surface waters, which these numerous and independent investigations establish, clearly show that the process of storage in large reservoirs must form a very important safeguard against the water-carriage of zymotic diseases. This safeguard, which is supplementary to and quite independent of that of filtration, has the great advantage of being under perfect control and much less liable to accidental disturbances than are most other methods of water-purification. It is, however, unfortunate that many reservoirs attached to water works have not been designed so as to secure the maximum advantages of storage, and their rearrangement with this object in view is generally a matter of great expense and sometimes impracticable. It is to be hoped that in future engineers will be more careful to arrange for such a circulation of the water that each particle of water entering shall remain as long as possible in the reservoir before passing out.

The influence of storage on the bacteriology of surface waters has recently been made the subject of very extended and interesting investigations by Houston in connection with the London water supply. There can be no doubt that adequate storage brings about the following beneficial changes:—

(1) Reduces the number of bacteria of all sorts.

(2) Reduces the number of bacteria capable of growing on agar at blood heat.

(3) Reduces the number of bacteria capable of growing in a bile-salt medium at blood heat.

(4) Reduces the number of coli-like microbes.

(5) Reduces the number of typical *B. coli.*

(6) Alters certain bacteriological ratios for river-waters, *e.g.* it reduces the number of typical *B. coli* to a proportionately greater extent than it reduces the number of bacteria of all sorts.

(7) If sufficiently prolonged, it devitalises the microbes of water-borne disease (*e.g.* the typhoid bacillus and the cholera vibrio).

(8) Reduces the amount of suspended matter.

(9) Reduces the amount of colour.

(10) Reduces the amount of ammoniacal nitrogen.

(11) Reduces the amount of oxygen absorbed from permanganate.

(12) Usually reduces the hardness and may reduce (or alter the quality of) the albuminoid nitrogen.

(13) Alters certain chemical ratios for river-waters; *e.g.* the colour results improve more than the results yielded by the permanganate test.

(14) Has a marked 'levelling' effect on the totality of water delivered to the filter-beds.

(15) Tends generally to lengthen the life of the filters (only under exceptional conditions is the contrary true).

(16) An adequately stored water is to be regarded as a 'safe' water, and the 'safety change' which has occurred in a stored water can be recognised by appropriate tests.

(17) The use of adequately stored waters renders any accidental breakdown in the filtering arrangements much less serious than might otherwise be the case.

The experimental basis for many of the above statements with regard to the benefits of storage will be found in the following table (Houston, Annual Report, March 31, 1910, p. 52):—

LONDON WATER SUPPLY.

Influence of storage shown by samples collected during 12 *months ending March*, 31, 1910 (*Houston*).

	No. of bacteria per 1 c.c.			*B. coli* (typical).									
	Gelatin 20—22° C. 3 days.	Agar 37° C. 2 days.	Tauro-Agar 37° C. 2 days.	c.c. 100 −	c.c. 100·0 +	c.c. 10·0 +	c.c. 1·0 +	c.c. 0·1 +	c.c. 0·01 +	c.c. 0·001 +	c.c. 0·0001 +	c.c. 0·00001 +	c.c. 0·000001 +
				p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.
Raw Thames water before storage	5268	495	63	0·5	0·5	6·3	26·9	52·9	12·8	—	—	—	—
Thames water after storage at Staines Reservoirs .	240	88	3	21·4	47·1	25·7	4·3	1·4	—	—	—	—	—
Thames water after storage at Chelsea Reservoirs .	442	63	8	41·3	28·0	21·3	9·3	—	—	—	—	—	—
Thames water after storage at Lambeth Reservoirs	354	54	8	20·8	43·0	31·9	4·2	—	—	—	—	—	—
Raw Lea water before storage . . .	37,071	837	86	0·0	0·5	6·3	31·4	39·7	13·2	7·3	0·5	0·5	0·5
Lea water after storage at Walthamstow Reservoirs	121	21	4	60·0	30·6	8·0	1·3	—	—	—	—	—	—

Fæcal streptococci in water. Attempts have been made to supplement the indications of fæcal contamination yielded by the presence of *B. coli*. The most recent and noteworthy of these is the examination of water for the presence of certain streptococci which are usually very abundant, sometimes even more abundant, in human fæces than is the *B. coli*. This matter has been engaging the attention of Dr. Houston since 1898, and he has recently (June, 1910) given a special account of the results, which he has obtained up to the present time.

At the outset it should be pointed out that these streptococci are not peculiar to human excreta, but are also abundantly present in those of the higher animals, many of Houston's experiments having been made with streptococci obtained from cow-dung. The study of these micro-organisms does not, therefore, at present put us in possession of that all important desideratum —a means of distinguishing between contamination due to the excrement of man and that which is due to the lower animals.

According to Houston, human fæces contain, roughly, 100,000 streptococci per 1 grm. On the other hand, in some stools streptococci are either absent or present in such small numbers relatively to those of other bacteria that search for them is useless. Their presence in water has hitherto been ascertained by spreading 1 c.c. of the water on a Drigalski-Conradi plate, on which medium, after incubation at 37°, the streptococci give rise to very minute colonies, which can then be sub-cultivated for determination of their biochemical characters.

Of 100 different cultures of streptococci obtained by Houston from sewage works fæces: (*a*) 100 produced acid in lactose and in raffinose media, and all of them clotted milk. (*b*) None reduced nitrates to nitrites. (*c*) Only four produced acid in a mannite medium. (*d*) 97 produced acid in a salicin medium. (*e*) 49 produced acid in a saccharose medium.

The grouping of these properties is best indicated by means of a convention similar to that employed in the case of *B. coli*, in which syllables are made to represent definite biochemical reactions, thus:—

la = acid in a *lac*tose medium.
ma = ,, ,, *man*nite ,,
mi = clot ,, *mi*lk ,,
ra = acid ,, *ra*ffinose ,,
sac = ,, ,, *sac*charose ,,
sal = ,, ,, *sal*icin ,,

The 100 streptococci examined may then be thus classified:—

la-mi-ra-sal	49
la-mi-ra-sac-sal	44
la-ma-mi-ra-sac-sal	4
la-mi-ra-sac	1
la-mi-ra	2

Thus 97 p.c. clotted milk, and produced acid in lactose, raffinose, and salicin media, and of these 48 produced acid and 49 no appreciable acidity in a saccharose medium.

During the year 1909 Houston examined the raw (unfiltered and unstored) Thames, Lea, and

New River waters for streptococci, employing 1 c.c. of each sample on Drigalski plates as above, with the following results :—

	No. of times streptococci were found in 1 c.c.
52 weekly samples of Thames water .	13
52 weekly samples of Lea water .	13
52 weekly samples of New River water	2

As regards the types of streptococci found in the above 28 samples of the 71 sub-cultures of streptococci examined the following combinations were found :—

	Thames	Lea	New River
La-ma-mi-ra-sac-sal.	1	2	0
La-ma-mi-sac-sal .	1	3	0
La-mi-ra-sac-sal .	9	17	0
La-ma-sac-sal .	0	1	0
La-ma-mi-sac .	0	3	0
La-mi-sac-sal . .	4	9	0
La-mi-ra-sac . .	2	10	0
La-sac-sal . .	0	1	2
La-mi-sal . .	0	1	0
La-mi-sac . .	2	0	0
La-ra-sac . .	0	3	0
Total	19	50	2

The above results are especially interesting as showing that the two impurer waters (Thames and Lea) contained streptococci much more frequently than the far purer water (New River), and further, that the streptococci actually discovered in the latter were of a type more remote from that of those which are usually discovered in fæces.

Bearing in mind that, on an average, upwards of 90 p.c. of the raw Thames and Lea samples, and about 50 p.c. of the raw New River samples contain typical *B. coli* in 1 c.c. or under, whilst in only 25 p.c. of the raw Thames and Lea samples, and in only 3·8 p.c. of the raw New River samples were streptococci found, it follows that the streptococci are a far less delicate index of contamination than the *B. coli*. The absence of streptococci in 1 c.c. of a water cannot, therefore, be regarded as any criterion of its purity. The relative scarcity of streptococci in waters which have undoubtedly received a considerable amount of sewage matters is accounted for by the fact, established by Houston, that streptococci very rapidly die off when placed in water. This circumstance points, of course, to the presence of streptococci serving as an indication of very recent contamination.

Recent bacteriological methods applied to other processes of water purification. From the evidence already brought forward it appears that confidence in the purification which can be effected by storage and sand-filtration, under favourable conditions, has been distinctly strengthened by the application of the more recent developments of bacteriological water examination—search for *B. coli* and other microbes more or less connected with sewage contamination.

Certain other processes of water-purification which are employed on the large scale may now be briefly considered.

Mechanical filters. The use of mechanical filters originated in America, and their employment in our own country is becoming more and more common. Such filters are in use at Bolton, Burnley, Heywood, Edinburgh, Crewe, Gloucester, Shrewsbury, and other places in Great Britain, whilst they have also been installed in India, Japan, and some of the colonies. Space does not permit the discussion of the relative merits of the two different processes of filtration. They each possess their advantages and disadvantages; they can each be made to yield good and bad results according to the manner in which they are employed. The following results may serve as an illustration of the very high degree of purification which *can* be secured by means of mechanical filters, which, in this instance, were employed to further purify a river water, which was being very imperfectly purified by some defective sand-filters.

Purification of River Water by Mechanical Filters.

	Number of Bacteria in 1 c.c.				*B. coli* (typical) in			
	Gelatin at 20° C.		Carbolic gelatin at 20° C. 7 days	Bile-salt agar at 37° C. 4 days	100 c.c.	10 c.c.	1·0 c.c.	0·1 c.c.
	2 days	7 days						
Raw river water . . .	3700	—	35	19	+	+	+	+
Ditto after passing sand filters	130	405	2	2	+	+	0	0
Ditto after further passing mechanical filters . .	8	33	0	0	0	0	0	0

Clark's process of softening. Already in 1885 the writer showed that in softening water with lime, a very large proportion of the bacteria are carried down with the precipitated chalk, but that if the latter is allowed to stand in contact with the softened water bacteria again pass from the precipitate into the water. In the softening process this removal of bacteria may, under favourable conditions, amount to upwards of 90 p.c.

Recently the writer had occasion to deal with a chalk well water, which was causing anxiety in consequence of its frequently containing *B. coli* in rather small volumes. The most obvious and unobjectionable method of purification which suggested itself was softening with lime, inasmuch as the water contained plenty of calcium bicarbonate in solution. The following table shows the results obtained in a number of small scale experiments in which this water was treated with lime, and sometimes with aluminoferric, and in which the softened water was sometimes decanted, sometimes filtered through paper without disturbing the precipitate ('clear filtration' in the table), and sometimes filtered after deliberately disturbing the precipitate ('turbid filtration' in the table):—

PURIFICATION OF WATER BY LIME AND ALUMINOFERRIC.

	Gelatin		*B. coli* in				
	No. of bacteria per 1 c.c.	Days incubated at 20° C.	100 c.c.	50 c.c.	10 c.c.	1·0 c.c.	0·1 c.c.
Raw well water	10 259	2 7	+	+	+	0	0
Ditto after filtration through sterile paper	7 236	2 7	+	+	+	0	0
Ditto+lime water, filtered through sterile paper after 1 hour's subsidence	0 90	2 7	+	+	0	0	0
Ditto+lime water and aluminoferric, filtered after 1 hour	0 39	2 7	+	0	0	0	0
Ditto+lime water; clear filtration after 3 hours	1 74	2 7	+	0	0	0	0
Ditto+lime water and aluminoferric; clear filtration after 3 hours	1 44	2 7	+	+	0	0	0
Ditto+lime water; turbid filtration after 3 hours	0 41	2 7	+	+	0	0	0
Ditto+lime water and aluminoferric; turbid filtration after 3 hours	0 41	2 7	0	0	0	0	0
Ditto+lime water; clear filtration after 25 hours	3 96	2 6	+	+	+	0	0
Ditto+lime water and aluminoferric; clear filtration after 25 hours	0 14	2 6	+	0	0	0	0

A great many experiments were made in addition to those recorded above, but always with the same disappointing result, that notwithstanding a large percentage reduction in the total number of bacteria taking place, it was only in rare cases that the *B. coli* was banished from 100 c.c. of the water by the precipitation process. It must be remembered that the demands now commonly made on a purification process with regard to the removal of *B. coli* are much more stringent than with regard to the removal of bacteria in general. Thus, should an untreated water contain 1000 bacteria per 1 c.c., if by treatment the number were reduced to 50 per 1 c.c., this would represent a purification of 95 p.c., and the water would be regarded as quite satisfactory from the point of view of the total number of bacteria present. But, if an untreated water contained the *B. coli* in 0·1 c.c., and after treatment this microbe were not present in less than 10 c.c., this would signify a removal of 99 p.c. of the *B. coli* present in the original water. But so high is the standard of purity at present often demanded in respect to freedom from *B. coli*, that the water which had thus been purified to the extent of 99 p.c. might still be regarded as of a questionable degree of purity.

OZONE TREATMENT OF WATER.

	Gelatin		*B. coli* in						
	No. of bacteria per 1 c.c.	Days incubated at 20° C.	100 c.c.	50 c.c.	10 c.c.	1·0 c.c.	0·1 c.c.	0·01 c.c.	0·001 c.c.
Chalk well-water +4 p.c. polluted canal-water	7000 10,000	2 7	+	+	+	+	+	+	+
Ditto after treatment with 5 times its volume of ozonised air during 2 hours; cultivations made 2 hours later	0 0	2 7	0	0	0	0	0	0	0
Chalk well-water +4 p.c. polluted canal-water	4000 7000	2 7	+	+	+	+	+	+	+
Ditto after treatment with its own volume of ozonised air during 24 minutes; cultivations made 1 hour later. (The ozonised air contained 0·23 p.c. ozone)	0 3	2 7	0	0	0	0	0	0	0

Purification of Water by treatment with Bleaching Powder.

Untreated chalk well water							Chalk well water after treatment with bleaching-powder						Millions of parts of water treated per 1 part of available chlorine used
No. of bacteria gelatin at 20° C.		B. coli in					No. of bacteria gelatin at 20° C.		B. coli in				
2 days	7 days	+ 100 c.c.	+ 50 c.c.	+ 10 c.c.	+ 1·0 c.c.	+ 0·1 c.c.	2 days	7 days	+ 100 c.c.	+ 50 c.c.	+ 10 c.c.	+ 1·0 c.c.	
First series of experiments													
98	640	+	+	+	0	0	17	83	+	+	0	0	1 part chlorine per 1 million
13	260	+	0	0	0	0	0	5	0[1]	0	0	0	1 part chlorine per 1 million
20	356	+	+	+	0	0	0	33	0[1]	0	0	0	1 part chlorine per 2 million
22	202	+	+	+	0	0	0	1	0	0	0	0	1 part chlorine per 2 million
13	539	+	+	+	0	0	0	9	0	0	0	0	1 part chlorine per 2 million
18	528	+	+	+	0	0	0	1	0	0	0	0	1 part chlorine per 2 million
9	315	+	+	+	+	0	0	4	0	0	0	0	1 part chlorine per 2 million
16	794	+	+	0	0	0	0	5	0	0	0	0	1 part chlorine per 4 million
9	152	+	+	0	0	0	0	2	0	0	0	0	1 part chlorine per 4 million
12	80	+	+	0	0	0	0	9	0	0	0	0	1 part chlorine per 4 million
14	115	+	+	0	0	0	0	10	0	0	0	0	1 part chlorine per 4 million
54	350	+	+	+	0	0	9	63	0	0	0	0	1 part chlorine per 8 million
17	116	+	+	+	0	0	12	37	0	0	0	0	1 part chlorine per 8 million
17	567	+	+	+	0	0	10	22	0	0	0	0	1 part chlorine per 8 million
—	—	—	—	—	—	—	8	38	0	0	0	0	1 part chlorine per 8 million
Av. 24	358						Av. 4	21					
Second series of experiments													
6	79	+	+	0	0	0	1	4	+	+	0	0	1 part chlorine per 1 million
1	105	+	0	0	0	0	0	3	0[1]	0	0	0	1 part chlorine per 2 million
6	353	+	0	0	0	0	0	0	0	0	0	0	1 part chlorine per 4 million
3	305	+	0	0	0	0	0	1	0	0	0	0	1 part chlorine per 4 million
1	129	+	+	0	0	0	0	3	0	0	0	0	1 part chlorine per 4 million
4	181	0	0	0	0	0	1	1	0	0	0	0	1 part chlorine per 4 million
5	244	+	+	0	0	0	0	0	0[1]	0	0	0	1 part chlorine per 4 million
0	111	+	+	0	0	0	0	9	0	0	0	0	1 part chlorine per 8 million
5	102	+	+	+	0	0	0	3	0	0	0	0	1 part chlorine per 8 million
1	181	+	+	0	0	0	0	15	0	0	0	0	1 part chlorine per 8 million
2	157	+	+	0	0	0	—	—	—	—	—	—	
9	289	+	+	0	0	0	0	1	0	0	0	0	1 part chlorine per 8 million
0	316	+	+	0	0	0	0	0	0	0	0	0	1 part chlorine per 8 million
1	120	+	0	0	0	0	0	6	0	0	0	0	1 part chlorine per 8 million
2	80	+	0	0	0	0	0	0	0	0	0	0	1 part chlorine per 8 million
Av. 3	183						Av. 0	3					

[1] *B. coli* found absent even in 500 c.c.

Ozone treatment. The bactericidal properties of ozone have been long demonstrated,[1] but it is only in quite recent years that it has been used on a large scale for the sterilisation of town water-supplies. In France the drinking waters of the towns of Nice, Chartres, and Cosne are being subjected to ozone treatment, whilst a plant for the treatment of 10 million gallons of water will be shortly erected in connection with the Paris waterworks. In Germany there are installations at Paderborn, Schierstein, and Hermannstadt.

The writer has recently made experiments with ozone in connection with the practicability of purifying the chalk well-water to which reference has just been made above. The extraordinary efficacy of this agent will be apparent from the foregoing results obtained in experiments in which the impurity of the chalk well-water was enormously exaggerated by the addition of 4 p.c. of polluted canal-water.

Bleaching-powder treatment. The bactericidal action of hypochlorites, again, has been long known, and bleaching powder is one of the oldest and commonest of disinfectants. The

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[1] Ohlmüller, Arbeiten a. d. Kaiserl. Gesundheitsamte, 1892, 229; van Ermengem, Ann. de l'Inst. Pasteur, 1895, 673; Ohlmüller and Prall, *loc. cit.* 1902, 417; Proskauer and Schüder, Zeitsch. Hygiene and Infectionskrankheiten, 41, 227, 243; 42, 293; Calmette, Ann. de l'Inst. Pasteur, 1899, 13, 344.

use of hypochlorites for the sterilisation of water-supplies was first brought into prominence in this country by Houston, who used 'Chloros' which is an electrolysed solution of common salt, for the treatment of the Lincoln water-supply during the memorable epidemic of typhoid which occurred in that city in 1904–5.[1]

The writer has recently had occasion to investigate the efficiency of the bleaching-powder treatment on a chalk well-water, the experiment being made with a large experimental plant.

From the results given on p. 734 it will be seen what a high degree of purification is obtained by this simple and inexpensive method of treatment, even when extremely small quantities of bleaching-powder are added to the water. Thus the only occasions on which *B. coli* was found even in 100 c.c. of the treated water was on the first day of each of the two series of experiments and thus when the apparatus had presumably not yet been completely washed out with treated water. On several occasions even 500 c.c. of treated water was examined for *B. coli*, and this microbe was on each such occasion found to be absent even in that large volume.

Similar results have been obtained by Sims Woodhead, Thresh, Hehner, Rideal, and others.

Treatment with ultra-violet light. The known bactericidal action of the ultra-violet rays has been applied by Victor Henri to the sterilisation of water on a large scale. The rays are supplied by a Cooper-Hewitt mercury lamp. The lamp is worked with 3 ampères at 220 volts, and is placed in the bend of a semi-circular trough through which the water is passed. At Marseilles the process has been tried with a plant yielding 130,000 gallons per 24 hours, and using 120 watts per 1000 gallons. The crude water always contained some *B. coli*, and the total number of bacteria varied between 30 and 300 per 1 c.c., whilst, in the treated water, *B. coli* was absent and the total number of bacteria was reduced to an average of 1 per 1 c.c. (Modern Methods of Water Purification, Don and Chisholm, London, 1911). *See* also W. Clemence, Engineering, Jan. 27 and Feb. 3, 1911.

Conclusions. During the 25 years that the systematic bacteriological examination of water has been practised an enormous amount of work has been carried out by a large number of investigators, but notwithstanding the immense multiplication of results it must be admitted that no very surprising novelties have been brought to light since the year 1895. By then all the salient features in the bacteriology of water had been mapped out, and the past 15 years have more especially been occupied in filling in countless details and in confirming over and over again what had already been broadly established.

Thus, already in the earlier period, the methods of bacteriology had been successfully applied to a determination of the value of the most varied processes of water purification natural and artificial, filtration, storage, precipitation, sedimentation, &c. It had been shown how such processes should, in the interests of public health, be continuously watched over and controlled by bacteriological examinations made at frequent intervals. Again, the vitality in water of the principal bacteria associated with water-borne zymotic disease had been investigated, and the results then obtained were substantially the same as those which have been arrived at by the most recent developments in bacteriological technique. In a word, these most recent developments in the methods of bacteriology have served to confirm and emphasise the conclusions which had been generally arrived at by the less perfect methods of the earlier period.

The all-important questions which the water-examiner has to answer are the same to-day as they have been all along: (*a*) has the water been contaminated with the excreta of man?; and (*b*) if such contamination has taken place, has the water in its subsequent history been subjected to conditions which would insure the destruction or removal of the pathogenic bacteria which may at any time be present in such human refuse?

To the first of these questions bacteriology cannot give a categorical answer even to-day, because we are not acquainted with any microbes which are absolutely characteristic of human excreta. The greatly increased facilities for the detection and quantitative determination of the *B. coli*, however, have undoubtedly placed us in a position to readily ascertain whether and to what extent a water has been contaminated with excremental matter irrespectively of whether the latter is of human or animal origin, but it is obvious that this will not, in general, carry us very far, inasmuch as practically all surface water *must* be more or less so contaminated.

To the second question a similarly qualified answer, again, can be readily given. If the water is free from *B. coli* in a large volume, it may safely be concluded that *a fortiori* it is free from the typhoid bacillus in a similar volume. But should the *B. coli* be found in a small volume, it does not follow that the water may at any time be liable to contain typhoid bacilli, because the discovery of the *B. coli* does not prove that the water has been contaminated by man at all.

Thus with regard to both questions, it is obvious that we are in a much stronger position in the matter of exculpating than in that of incriminating a water. However, the inference that a water free from *B. coli* in a large volume is, therefore, necessarily a safe one, requires a slight qualification in view of the remarkable and interesting revelations which have in recent years been made with regard to what are known as '*typhoid carriers*.' Some of these persons suffering from ambulatory typhoid discharge typhoid bacilli in the urine, and it is thus possible that water may actually become contaminated with typhoid bacilli without at the same time receiving any *B. coli*. Although this is not likely to be of frequent occurrence, still its possibility, especially in the case of men working in wells, filter-beds, and service reservoirs, should on no account be disregarded.

Certainly one of the most important advances made in bacteriology during recent years is the careful characterisation of bacteria by means of biochemical tests, and the isolation of particular types of bacteria from such mixtures as

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[1] In that epidemic there were as many deaths (119) from typhoid in six months as had occurred from the same cause during the previous eighteen years.

are present in water by means of special culture-media, liquid and solid. However, until bacteriologists have agreed upon uniform tests for each particular microbe it is unavoidable that there should be much confusion and that the results obtained by different observers should be difficult to compare. Under these circumstances the interpretation of results by the individual observer is a matter of the greatest importance, and it is needless to say that unless the individual observer has a wide personal experience and a thorough knowledge of the factors affecting the purity of water-supplies of different kinds his interpretation of the results obtained will not only have little practical value but may easily lead to very serious mistakes.

Thus, whilst the outstanding achievement in bacteriological water examination during the past 15 years is the systematisation of tests for detecting the presence in water of specific bacteria, especially *B. coli*, Streptococci, and the spores of *B. enteritidis sporogenes, the different possible sources of these bacteria, and their different hygienic significance according to source* render any hard and fast application of standards based on the presence of these microbes impossible without liability to serious errors of judgment being committed.

Space has not permitted reference in detail to the spores of *B. enteritidis sporogenes*[1] as an index of fæcal contamination. The figures on p. 726 show how much less abundant in fæces are these spores than is the *B. coli communis*. They do not, therefore, form such a delicate test for sewage contamination as does the *B. coli*, and their final identification is much less certain. The water-bacteriologist should, however, not neglect a search for these spores, but should regard the evidence which their presence or absence affords as supplementary to that which is furnished by the *B. coli* results.

In conclusion a word may be said with regard to the relative value of the chemical and bacteriological examination of water. At the present time it is often supposed that the chemical has been entirely superseded by the bacteriological examination, and that the chemical analysis of drinking water can be dispensed with. In reality the two methods of examination supplement each other. In those cases in which the source and general characters of a water supply are well known, the variations in purity from day to day or from week to week can undoubtedly be more satisfactorily watched by means of bacteriological examination. On the other hand, it is often desired by means of a single examination to ascertain the fitness or otherwise of a water for domestic use, and in such cases the omission of a chemical analysis may lead to an entirely erroneous opinion being formed. The ingredients detected by chemical analysis—organic matter, ammonia, nitrates, chlorides, &c.—on which an opinion as to hygienic quality is based, are all much more permanent and uniform features in the composition of the water than are the amount and the nature of the bacterial life which it may contain. The chemical analysis will, therefore, if skilfully interpreted, enable a much better idea of the potability of the water to be obtained than would be possible from a single bacteriological examination.

There are so many factors and considerations which have to be taken into account if an opinion of any real value as to the hygienic quality of water is to be formed, that no knowledge or information which can be gained either by chemical, or by bacteriological examination, or by inspection of source, or by any other available means whatsoever should be neglected.

P. F. F.

WATER-GAS *v.* Gas, water.

WATER GLASS. *Soluble glass v.* Glass.

WATER-OF-AYR STONE *v.* Whetstone.

WATERS, AERATED *v.* Aerated waters.

WATER STONES *v.* Agate.

WAVELLITE. A mineral consisting of hydrous aluminium phosphate $3Al_2O_3{\cdot}2P_2O_5,12H_2O$, forming globular or stalactitic masses with an internal radiating structure. The colour is white, yellowish, or green; sp.gr. 2·32. The mineral usually occurs on the joint faces of slaty rock, and was first observed in the eighteenth century by Dr. W. Wavell in the slates at Filleigh near Barnstaple in Devonshire. Good specimens have also been found in Co. Cork. In larger amounts it occurs in Arkansas and Pennsylvania. At South Mountain in Pennsylvania it has been mined as a source of phosphorus, used locally for making matches. L. J. S.

WAX VARNISH *v.* Varnish.

WAXES, ANIMAL AND VEGETABLE. These waxes are a group of substances resembling beeswax in their physical properties, and are mixtures of compounds composed of the elements carbon, hydrogen, and oxygen. Waxes of mineral origin such as paraffin wax, ozokerite, ceresin, and montan wax are described elsewhere. The chief proximate constituents of the waxes are: (1) esters of fatty acids with alcohols containing a high number of carbon atoms; (2) esters of fatty acids with glycerol, thus palmitin and myristin seem to impart wax-like properties to some of the substances containing them; (3) free fatty acids; (4) free alcohols containing a large number of carbon atoms; (5) hydrocarbons. The formulæ assigned to the compounds with large molecules must be regarded as somewhat uncertain and may be altered by further investigations. Physically the waxes come in the series: (1) fixed oils; (2) soft fats; (3) tallow-like substances and solid fats; (4) waxes; and (5) resins. An explanation of the terms *saponification value*, *iodine value*, and *acid value* will be found in the article on Oils, fixed, and fats. Many of the waxes are difficult to saponify, and require special treatment to effect this. Descriptions of the more important and better-known waxes are given below. References: Schaedler, Technologie der Fette und Oele; Benedikt-Ulzer, Analyse der Fette und Wachsarten; Lewkowitsch, Chemical Technology and Analysis of Oils, Fats, and Waxes; Allen, Commercial Organic Analysis, vol. ii., Fixed Oils, Fats, and Waxes; Cowan, Waxcraft.

Arjun wax (*White insect wax of India*). About the year 1786 a wax produced by an insect was noticed in Madras, and it was thought that it might resemble the insect wax of China, but it appears to be different. The insect has been

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[1] Klein. Local Government Board: Medical Officer's Reports, 1897–8, 1898–9, 1901–2; Klein and Houston, *ibid.* 1899–1900; Hewlett, Trans. Jenner Institute, Series II, 70; Journ. State Medicine, 1904, 12, 108.

named *Coccus ceriferus*, and also *Ceroplastes ceriferus*; it is found on the twigs of *Terminalia Arjuna* (Wright and Arn.) and several other trees; it is not, however, at all abundant. The wax occurs on the twigs in small mounds of a dull buff colour; its m.p. is given as from 55° to 63°, and its sp.gr. as 1·04 at 29°. It is moderately hard and brittle, and has a somewhat pleasant smell. It is partially soluble in cold alcohol, and almost completely soluble in boiling alcohol; it dissolves freely, but not entirely in benzene and in ether; it is only sparingly soluble in oil of turpentine and in carbon disulphide. In composition it corresponds to the formula $C_{13}H_{26}O$ (Pearson, Phil. Trans. 1794, 84, 383; Indian Museum Notes, 1891, 2, 91).

Balanophore wax is derived from the parenchymatous cells of *Langsdorffia hypogæa* (Mart.), a native of Brazil, and of *Balanophora* species (a native of Java and the neighbouring islands); which are parasitic plants some 5 or 6 cm. long, growing on the roots of other plants. These plants are so rich in wax that they can be set on fire and burn with a luminous flame, and torches can be made by coating wooden sticks with the plant made into a paste.

By boiling the plant the wax is procured as a greyish and yellowish mass. Ether extracts it from the plant, and as thus obtained it has the colour and consistence of natural beeswax; it melts at about 100°, has a sp.gr. of 0·995 at 15°, and is easily soluble in ether, and only very sparingly soluble in alcohol. The wax has the property of dissolving in cold sulphuric acid and being reprecipitated by water. It is a resinous wax, and also contains a glyceride (Schaedler).

Beeswax is produced by the common bee *Apis mellifica*, and also by some allied species; it is not collected from the flowers by the bee, but is the secretion of certain organs situated on the underside of the abdomen of the neuter or working bees, and is used by them in forming the cells of the honeycomb. They are said to consume about 10 lbs. of honey in order to secrete 1 lb. of wax. The honey is allowed to run out from the comb, which is then pressed to separate as much honey as possible. The adhering honey and other impurities are next removed by melting the mass in hot water; the melted wax floats on the surface, and is strained to remove dead bees and brood. The residue is put in layers with straw, and is pressed to obtain more wax, the straw acting as a filter; this product is known as 'press wax.' The mass then remaining is sometimes extracted with benzene to obtain still more wax, the product being 'extraction wax.' The 'extraction wax' is apt to be impure from the use of artificial comb, and also from substances being extracted from the dead bees and straw; further, wax compositions and adulterated beeswax are also sold under the name of 'extraction wax' (Hirschel, Chem. Zeit. 1904, 28, 212). A common practice is to pare off the capping of the honey cells and then place the comb in a centrifugal machine, which removes the honey and leaves the comb undamaged, so that it can be replaced in the hive to be refilled by the bees, and thus save the honey that they would use to produce fresh wax. In this system the capping only is melted down for wax.

Beeswax is yellow in colour and varies in tint, according to the materials employed by the bees and the care taken in its preparation; sometimes it is brownish, reddish, or greenish. It has a pleasant honey-like smell, which is made more apparent by warmth. When cold it is brittle; at ordinary temperatures it is tenacious; its fracture is dry and granular. The sp.gr. at 15° is from 0·958 to 0·975, that of melted wax at 98°–99° compared with water at 15·5° is 0·822. It softens when held in the hand, and melts at 62°–66°; it solidifies at 60·5°–63°. The chief components of beeswax are myricyl palmitate $(C_{30}H_{61})C_{16}H_{31}O_2$, free cerotic acid $C_{26}H_{52}O_2$, and hydrocarbons (Schwalb, Annalen, 1886, 235, 106). It is insoluble in water, cold alcohol dissolves very little, boiling alcohol dissolves a good deal, leaving an undissolved residue from which, however, something is dissolved every time the treatment with boiling alcohol is repeated. The soluble portion was called *cerin*, and the less soluble residue *myricin* by J. F. John (Chem. Tabellen der Pflanz. 1814, 42); he first separated the wax of *Myrica cordifolia* (Berg.), from Cape Colony, into a soluble and an insoluble portion, and then separated beeswax in the same way, and gave the products these names. The cerin and myricin from beeswax and from *M. cordifolia*, however, must not now be regarded as identical; the latter wax seems not to have been examined recently and probably would be found to resemble myrtle wax in its composition. Brodie (Phil. Trans. 1848, 147; 1849, 91) found a new acid free in the soluble part of beeswax, and named it *cerotic acid*; and in the myricin or insoluble part he found an ester of palmitic acid with a wax alcohol, which he called *melissin* (now called *myricyl* or *melissyl alcohol*). The dissolved substances are deposited when the alcohol cools. Beeswax is said to dissolve in about 300 parts of boiling alcohol, leaving only a small amount of yellowish-brown residue. Warm ether dissolves it readily, part being deposited on cooling. Buchner (Chem. Zeit. 1907, 31, 570) allowed beeswax to soak in ether at the ordinary temperature for some time, filtered the resulting homogeneous paste, and washed it with ether; after getting rid of the ether he obtained from the filtrate 30 p.c. of a fairly soft, deep yellow mass, and from the insoluble residue 70 p.c. of a bright brownish wax, considerably harder than the original wax. The soluble portion had an acid value of 40, and a saponification value of 83·8, whilst the insoluble portion had an acid value of 11·6, and a saponification value of 99·1; thus the cerotic acid and colouring matter dissolve in cold ether in higher proportion than the myricyl palmitate.

Other solvents are fixed oils, carbon disulphide, chloroform, and oil of turpentine. Cerotic acid is soluble in hot alcohol, but separates almost completely on cooling; its presence in beeswax probably increases the solubility of the myricin. Beeswax contains about 12–16 p.c. of free cerotic acid, but this probably includes some other acids. From 11 to 17·5 p.c. of hydrocarbons have been found in genuine samples of beeswax. Indian Ghedda wax contains less, only 8·6 p.c. having been found (Buchner, Chem. Zeit. 1905, 29, 79). Artificial comb containing added paraffin wax is sometimes used in the hives, and then the percentage of hydrocarbons in the wax is increased. Minor constituents and colouring matter are also present; the latter remains dissolved when the hot alcoholic solution cools. Berg. (Chem. Zeit. 1908, 32, 777) found at least 0·6 p.c. of cholesterol esters and probably considerably more, which are hard to saponify and have high saponification values; he separated also small quantities of various acids, one of them having the specific odour of beeswax. The acid value of yellow beeswax is from 17 to 23; the saponification value is from 88 to 107; and the iodine value is from 6 to 14, thus showing the presence of unsaturated compounds. Some varieties of beeswax vary in composition even more than appears above, especially those from China and India, the latter including that known as Ghedda wax (Buchner, Chem. Zeit. 1901, 25, 21, 39; 1905, 29, 33; 1906, 30, 528; Buchner and Fischer, Zeitsch. öff. Chem. 1913, 19, 147). Ghedda or East Indian wax has been examined by Lipp and Kuhn (J. pr. Chem. 1912, 86, 184), who found that it contains only one alcoholic radicle, namely ceryl, present chiefly as ester, thus differing from ordinary beeswax, which contains chiefly myricyl ester with only a little ceryl ester; the ester acids also differ from those of ordinary beeswax, but the hydrocarbons are the same, namely $C_{26}H_{54}$ and $C_{30}H_{62}$.

Indian beeswax is derived from three species of bees: *Apis dorsata*, *A. indica*, and *A. florea*, but chiefly from *A. dorsata* (*A. mellifica* does not occur there except as an importation). The wax from the combs of these three species is substantially of the same composition. It differs from European beeswax in having a lower acid value; in the case of 34 specimens from these 3 species the acid value ranged from 4·4 to 10·2, with an average of about 7, the saponification value from 75·6 to 130·5, and the Hübl iodine value from 4·8 to 11·4. Some Indian waxes of unknown origin gave higher acid values, and other values outside these limits. Turmeric is used to give a golden-yellow colour to the wax. Another kind of beeswax is produced in India from a small stingless bee known as the dammar bee, *Melipona* or *Trigona* species; this wax is of a blackish colour, and sticky consistency. In 8 specimens the acid value ranged from 16·1 to 22·9, the saponification value from 73·7 to 150, the iodine value from 30·2 to 49·6, and the m.p. from 66° to 76° (Hooper, Agricultural Ledger, 1904, 11, 73).

A wax called *Andaquies wax* is collected by the Indians in Colombia, especially by the Tamas tribe, which lives near the Rio Caqueta. It is probably the product of small *Melipona* bees. A sample was examined by Lewy (Ann. Chim. Phys. 1845, [iii.] 13, 453); after purifying it by treatment with boiling water he found that its m.p. was 77°, its sp.gr. at 0° was 0·917, and that it contained 81·66 p.c. of carbon and 13·55 p.c. of hydrogen. It is used locally for making candles for religious worship.

White beeswax. Yellow beeswax is not adapted to candle-making, as candles made from it burn badly and with a smoky flame. It is purified by repeatedly re-melting in hot water until it is no longer grey, and any remaining honey is removed. In doing this the grey underlayer is cut off, and re-melted with the raw wax. Dilute sulphuric acid is sometimes added to the water to diminish the tendency of the wax and water to form an emulsion.

The next step is to destroy the yellow colouring matter. Chlorine and many other bleaching agents attack the wax and make it more brittle and friable, and thus cause it to lose its softness, and tallow has to be added to restore it. Chlorine further forms chloro substitution products with the wax, and hydrogen chloride is liberated when the candle is burnt.

The best method of bleaching is to reduce the wax to thin strips or shavings so as to increase the surface as much as possible, and to expose it to moisture and sunlight. The melted wax is poured from a ladle into a square box of metal plate, in the bottom of which are several narrow slits. These slits are directly over a horizontal wooden roller revolving in a vessel filled with water which covers half the roller. The wax escapes from the slits in bands, which pass over the revolving roller and solidify in the water in the form of thin ribbons.

Another plan is to melt the wax in a rotating vessel of tinned copper provided with taps; from these the wax falls in drops or streams into ice-cold water. The grains or threads expose more surface, and the bleaching takes at least one-third less time, than when ribbons are used.

These ribbons, threads, or grains are removed from the water and spread on linen stretched over square wooden frames, and then exposed to the sun. Every day they are once or oftener sprinkled with water to keep them moist, and they are frequently turned over to expose fresh layers to the sun. After a longer or shorter period, depending on the intensity of the sunshine and the temperature, the bleaching is complete.

The wax is then once more melted in hot water, strained, and allowed to solidify in suitable shapes. The inner portion of the ribbon bleaches much more slowly than the outer surface, and the bleaching occupies 20–35 days or more. To accelerate the bleaching the partially bleached wax is re-melted and again made into ribbons so that new surfaces are exposed; this causes loss of from 2 to 10 p.c. Thread and granular wax rarely require re-melting. Wax from different sources bleaches with varying facility, and some cannot be bleached, so it is well first to try a sample on a small scale.

Since the sun-bleaching is probably due to the formation and action of either ozone or hydrogen peroxide, the action can be aided by melting together from 1 to 1½ parts of rectified oil of turpentine, free from resin, with 8 parts of yellow wax, and then making into ribbons, and proceeding as above; this reduces the time some 6 or 8 days, at the end of which the smell of turpentine will have disappeared. Sometimes a few per cent. of tallow are added to the wax to hasten the bleaching.

Wax bleachers frequently make additions to the wax—such as argol, alum, white arsenic—which, however, seem to have no great value. They are removed on re-melting the wax with water; or else additions of tallow, vegetable waxes, stearic acid, &c., are made to increase the whiteness of the wax after bleaching.

Wax in threads and grains can be bleached by immersion in hydrogen peroxide, and also by treatment with sodium hypochlorite, or dilute chromic acid or a mixture of potassium dichromate and sulphuric acid, but the products are not suitable for some purposes. Animal charcoal can also be used to decolorise it.

White wax is comparatively hard and brittle, with a splintery fracture, translucent at the edges; its solubility in the various media, its proximate and ultimate composition, are nearly the same as those of yellow wax, but the physical properties and chemical values are somewhat altered by the process of bleaching.

Beeswax, both white and yellow, is liable to adulteration. The substances used are: water; powders such as yellow ochre, clay, brickdust, kaolin, gypsum, barium sulphate, litharge, sulphur, pea flour, starch and flour (but small quantities of starch and flour may occur in genuine wax that has been rolled or pressed, as the rollers or presses are dusted with flour to prevent the wax from sticking); carbon compounds such as tallow, wool fat, spermaceti, insect wax, stearin, stearic acid, resin, paraffin wax, ceresin, ozokerite, and various plant waxes. Methods of examining wax for adulterants will be found in: Lewkowitsch's Chemical Technology and Analysis of Oils, Fats and Waxes, 1909; Allen's Commercial Organic Analysis, vol. ii. 1910; Foods and Food Adulterants, U.S. Dept. Agric., Chem. Div., Bulletin No. 13, pt. vi. 1892; (this contains a very full bibliography, which is abstracted in J. Soc. Chem. Ind. 1892, 11, 756); and in various original papers.

Candelilla wax is obtained from plants growing in great quantities in northern Mexico and the southern parts of the United States; attention was called to the wax on these plants by Sanders in 1905. The analytical results published about it vary widely, and samples of wax called by this name possibly come from different plants, and may also vary with the age of the plants and the time of year at which they were gathered; the mode of preparation, and the presence of water in the wax may also account for some variations. *Euphorbia cerifera* (Alcocer), *E. antisyphilitica* (Zucc.), and *Pedilanthus Pavonis* (Boiss.) have been given as the plants from which the wax was obtained.

The wax occurs as an excretion covering all parts of the plant except the roots; it can be obtained by boiling the plant with water and skimming off the layer of melted wax; the pieces of plant must be kept from rising by wrapping them in wire cloth or by tying them in bundles and weighting these down. Another plan is to subject them to live steam, which melts off the wax, which can be easily separated from the condensed water. It can be purified by re-melting and straining or filtering through animal charcoal in steam-jacketed iron filters. The yield is from 2½ to 5 p.c. of the dry plant. The wax varies in colour from light greenish-yellow to almost chocolate-black; it can be bleached sufficiently to compare with carnaüba wax. It is harder and more brittle than beeswax, but not so hard nor so brittle as carnaüba wax; at first sight it appears more like a resin than a wax.

The following are some of the analytical values recorded: m.p. 66°–80°; sp.gr. 0·9820–0·9856 at 15°/15°; refractive index at 85° 1·4545–1·4626; acid value 12·4–19·0; saponification value 35·0–86·5; Reichert-Meissl value 0·53–7·69; iodine value 14·0–20·4; unsaponifiable matter 76·7–77·3 p.c.; hydrocarbons 42·5–59·7 p.c. Hydrocarbons with formulæ near to that of hentriacontane $C_{31}H_{64}$ seem to be present. The winter wax is thought to have the highest melting-point, density, acidity, and proportion of hydrocarbons. Sanders (Chem. Soc. Proc. 1911, 27, 250) states that a sample of the wax prepared in January from plants collected in Coahuila was greenish-white, and contained a considerable proportion of water. When freed from this it was dark brown, and gave the following values: m.p. 67·5°; sp.gr. 0·9850; acid value 14·39; saponification value 46·76; iodine value (Hübl) 16·60; unsaponifiable matter 77·00 p.c.; and hydrocarbons 48·60 p.c. He states that it contained hentriacontane and myricyl alcohol. Olsson-Seffer (Imp. Inst. Bull, 1909, 7, 411) and other analysts give some values which do not fall within the limits mentioned above.

The wax is soluble in oil of turpentine, chloroform, ether, benzene, carbon disulphide, and acetone when hot; it dissolves partially in boiling alcohol, but the greater part separates on cooling. A mixture of 3 parts of absolute alcohol and 2 parts of 90 p.c. benzene was found to be an excellent solvent for it when hot. It can be used for making varnishes, insulating materials, shoe polishes, floor polishes, dental moulding compositions, sealing wax, lithographic inks, waterproof papers, lacquers for metals, and also to raise the melting-point of cheaper waxes for the manufacture of candles and matches. Several factories are engaged in preparing it in Mexico, and it is coming into European commerce. Further references are: Sanders, Anal. Inst. Med. Nac. Mexico, 1905, 7, 498; La Candelilla, pubd. by Instituto Medico Nacional, Mexico, 1910; Hare and Bjerregaard, J. Ind. and Engin. Chem. 1910, 2, 203; Fraps and Rather, *ibid.* 454; Niederstadt, Analyst, 1911, 36, 598; and Chem. Zeit. 1911, 35, 1190; Imp. Inst. Bull. 1912, 10, 128.

Cape berry wax. Samples of this wax have been shown at exhibitions in London, and it is capable of being collected in quantities in Cape Colony, but it has not yet come into any extensive use. It is probably derived from one of the species of *Myrica* growing in South Africa, which include *M. quercifolia* (Linn.), *M. cordifolia* (Linn.), and *M. serrata* (Lam.); it is similar to myrtle berry wax in its general characters and in its physical and chemical properties, which were found to be: sp.gr. 0·874 at 99°; m.p. 40·5°; m.p. of the fatty acids 47·5°; mean molecular weight of the fatty acids 236·1; acid value 4·1; saponification value 211·1; iodine value 1·1. It yields a hard white soap, but does not seem to be suitable for candle making (Imp. Inst. Bull. 1906, 4, 300). The results of another examination are: sp.gr. 0·9893; m.p. 49°; refractive index at 80° 1·4364; acid value 2·5; saponification value 212·3; iodine value 2·03; unsaponifiable matter 2·51 p.c.; fatty acids 89·7 p.c.; m.p. of mixed fatty acids 48·5°; solidifying-point of these 46·5°; mean molecular weight of these 241·4; it was described as South African berry wax, and was pale greenish-grey with a granular fracture; when melted it formed a greenish-brown muddy liquid, and it was filtered before examination (Cocking, Chem. and Drug. 1908, 73, 74).

Carnaüba or **carnahuba wax** is derived from the carnaüba palm, *Copernicia cerifera* (Mart.) (*Corypha cerifera*, Linn.), which grows in Brazil, especially in the provinces of Ceara, Rio Grande do Norte, and Piauhy. The trunk is 25–35 ft. high with a crown of leaves at the top. The young leaves of about 3 ft. long have a coating of wax on both the upper and under sides, which appears homogeneous to the naked eye. The wax layer is thicker on the upper side, and comes off in scales; on the lower side it is thinner and more adherent. The harvesting extends over the six dry months of the year, and the leaves are cut twice a month, about eight leaves being cut from a palm at a time, those leaves that have reached a certain stage of development being taken, leaving the very young leaves to develop later. If the leaves are allowed to become too old the wax is easily detached, and is lost before the leaves are brought to the ground. The leaves are spread out to dry, and are then slit up with a knife and beaten over a cloth to detach the wax, which comes off in scales or as a greyish-white powder. A little water is added to the powder, and it is melted and poured into moulds, in which it solidifies in cakes of about 2 kilos. About 850 leaves give 16 kilos. of wax; about 1·8 kilos. of wax, valued at 1*s.* 6*d.*, are obtained from one palm. On poor land 1200 leaves, and on good land only 500 leaves are required to give the 16 kilos. In some estimates, however, the yields are not so good as these.

In the year 1908 the exports of carnaüba wax from Brazil amounted to 2,592,027 kilos., with a value including cost, insurance, and freight of £242,243; in 1907 the exports were 2,778,801 kilos. with a value of £418,600.

Raw carnaüba wax is of a dirty yellowish or greenish colour, amorphous, hard, brittle, and easy to powder. In its outward appearance it is compact, but penetrated with very many air spaces; it is tasteless, and smells, when fresh, somewhat like fresh hay—*i.e.* of coumarin; later it becomes inodorous. It is purified by remelting, and has then a greenish-yellow or straw-yellow colour. The m.p. is variously given as from 83°–86°, and an old specimen melted at 90°–91°. In preparing bleached carnaüba wax, a certain amount of paraffin wax is added, such wax consequently has a lower melting-point. The wax, especially when fresh, on melting diffuses a slight odour, which is not unpleasant; on distillation it gives a paraffin-like product. The sp.gr. is 0·990–0·999 at 15°. The acid value is from 0·3 to 8·0; saponification value 78–88·3; and iodine value 7–13·5.

The composition has been very fully examined by Stürcke (Annalen, 1884, 223, 283); he found that the principal constituent is the myricyl ester of cerotic acid ($C_{27}H_{53}O_2{\cdot}C_{30}H_{61}$), or as the free acid was not crystalline, it may perhaps be the ester of an isomeride closely resembling cerotic acid; that it contains a considerable quantity of free myricyl alcohol $C_{30}H_{61}OH$; and that minor constituents isolated after saponification, are: (1) a hydrocarbon with m.p. 59°–59·5°; (2) an alcohol $C_{26}H_{53}{\cdot}CH_2OH$ with m.p. 76°; (3) a dihydric alcohol $C_{23}H_{46}(CH_2OH)_2$ with m.p. 103·5–103·8°; (4) an acid $C_{23}H_{47}{\cdot}CO_2H$ with m.p. 72·5°, isomeric with lignoceric acid; and (5) the lactone $C_{19}H_{38}{<}{\genfrac{}{}{0pt}{}{CH_2}{CO}}{>}O$ with m.p. 103·5°.

When the wax is extracted with boiling alcohol the myricyl alcohol dissolves together with a small amount of the myricyl ester, and these constituents separate when the alcohol cools; if the extraction is continued the later extracts remove small quantities of the ester, which is only very slightly soluble in boiling alcohol, the last extracts containing less than a gram per litre. The wax is not easily saponified; Berg (Chem. Zeit. 1909, 33, 885) recommends the use of xylene as a solvent for this purpose.

Carnaüba wax when mixed with paraffin, ceresin, beeswax, &c., increases their hardness and gives a peculiar lustre; it also raises their melting-points. It is used for making hard candles, leather polishes, and certain varnishes. It is bleached by melting and filtering through animal charcoal, but some paraffin wax is added to facilitate the process, and this lowers the melting-point of the bleached wax. Another use of the wax is for making Edison's phonograph cylinders.

References.—Brande, Phil. Trans. 1811, 261; Bérard, Bull. Soc. chim. 1868, 9. 41; Story Maskelyne, J. Chem. Soc. 1869. 22. 87; von Pieverling, Annalen, 1876, 183, 344; Stürcke, *ibid.* 1884, 223, 283; Valenta, Zeitsch. anal. Chem. 1884, 23, 257, the melting-points of mixtures of the wax with other substances; Liebermann, Ber. 1885, 18, 1979, a substance isolated from the wax; Schaedler, Technologie der Fette und Oele, 1892, 881; Gascard, J. Soc. Chem. Ind. 1893, 955; Villon, Bull. Soc. chim. 1893, [3] 9, 1046, the bleaching and uses of the wax; Kebler, J. Soc. Chem. Ind. 1894, 13, 745, the constants of the wax; Brannt, Fats and Oils, 1896, 144; Semler, Tropische Agrikultur, 1897, i. 732; Lewkowitsch, Analyst, 1899. 321, acetyl values; Eichhorn, J. Soc. Chem. Ind. 1901, 20, 74, saponification method; Radcliffe, *ibid.* 1906, 25, 158, the constants of the wax; Engler, Chem. Zeit. 1906, 30, 711. the rotatory power; Lewkowitsch, Oils, Fats and Waxes. 1909, ii. 736; Berg, Chem. Zeit. 1909, 33. 885; and Analyst, 1909. 445, saponification method.

Cochin China wax (*Cay Cay fat, Irvingia butter*). This is obtained from the fruit of the Cay Cay tree, *Irvingia Oliveri* (Pierre), a forest tree reaching the height of 100 ft., and growing widely in the east of Cochin China. The fruit is the size of a lemon, the endocarp has the size and shape of an almond with its outer covering. and the kernel, too, resembles in size and shape that of the almond. The fruits are ripe in July. and fall to the ground; they are gathered into heaps by the natives, and left for two months to allow the soft outer parts to decompose; they are then carried to the houses and dried in the sun. They are opened with a strong knife, and the kernels are removed, dried in the sun, and pounded in a mortar. The pulp is placed in a vessel having a bottom of plaited material; this is fixed above water in another vessel, and the water is heated, but not to boiling. When the pulp has become a sticky paste it is wrapped in a mat of rice straw, and submitted to pressure in a crude press, the operations being repeated several times, and the melted wax is either allowed to solidify in moulds or else is cast into candles in bamboo tubes. In the laboratory the dry kernels extracted with carbon disulphide gave 52 p.c. of wax. The wax is of a greyish-yellow colour, and is unctuous to the touch. The purified wax softens at 37°, melts at 38°, and solidifies at 34° (Vignoli, Le Cay Cay, Thèse présentée à l'Ecole Superieure de Pharmacie de Montpellier, 1886).

Bontoux (Les Matières Grasses, 1908, 1276; J. Soc. Chem. Ind. 1909, 28, 429) found that 100 dry seeds weighed 360 grms. and gave 78 p.c. of shells and 22 p.c. of kernels. The latter, on extraction with light petroleum, gave 60·45 p.c. of wax. The wax had the consistency and texture of beeswax, and was more brittle, with the same conchoidal fracture; its sp.gr. at 40° compared with water at 40° was 0·913; it melted at 39·7° in a capillary tube, and solidified at 31°; its acid value was 0·86; saponification value 235·3; unsaponifiable matter 0·42 p.c.; iodine value 6·7; Reichert-Meissl value 0·62. The insoluble fatty acids, together with the unsaponifiable matter were 94·0 p.c., their m.p. was 38·8°; solidifying point (titer test) 36·6°; neutralisation value 250·2; and mean molecular weight 224. Two samples of the wax of native origin had nearly the same values, but the acid values were 23·5 and 34·9, which, however, are not excessive, and they contained 0·16 p.c. and 0·19 p.c. of unsaponifiable matter. Bontoux prepared methyl esters, and concluded that the wax was mainly composed of myristin 60–65 p.c., laurin 30–35 p.c., and about 5 p.c. of olein. The wax gives a hard white soap. The production in Indo-China has declined, owing to the introduction of petroleum. A Cay Cay wax is also obtained from the fruit of the tree *Irvingia malayana* (Oliver), which grows in Cambodia. Other references are: Heckel, Annales de l'Institut colonial de Marseille, 1893; Apoth. Zeit. 1898, 169; Crevost, Les arbres à suif de l'Indochine, Hanoi, 1902; Bulletin économique de l'Indochine, Hanoi, 1902.

Cow tree wax (*Milk tree wax*). In the north of Venezuela, in the neighbourhood of Caracas and of Lake Maracaibo, and in the valley of Caucagua, there grows a tree (*Brosimum Galactodendron*) called *Palo de vaca* or *Arbol de leche*, which yields a thick milk when incisions are made in its trunk; this is drunk like milk by the inhabitants. This milk, when heated, forms a skin, and if this is removed and evaporation continued, an oily liquid is obtained, together with a fibrous mass. The oily liquid when it has solidified, is a yellowish-white, hard translucent wax; it begins to melt at 40°, and is completely melted at 60°. It is insoluble in water, but is easily dissolved by essential oils. It dissolves in boiling alcohol and separates on cooling; it is saponifiable by caustic potash. It can be used like beeswax for making candles. Humboldt, Ann. Chim. Phys. 1817, 7, 182; Boussingault and Mariano de Rivero, *ibid.* 1823, 23, 219; Marchand, J. pr. Chem. 1840, [i.] 21, 43.

Fig tree wax (*Gondang* or *Kondang* or *Getah wax, Java* or *Sumatra wax*). This wax is obtained in Java from the milky juice which runs from incisions made in the bark of the gondang, a wild fig tree (*Ficus variegata*, Blume. = *F. ceriflua*, Jungh. = *F. subracemosa*, Blume.). The juice is boiled with water until the wax separates. It forms a fairly hard cake, cream coloured within, turning brown in the air; it has a conchoidal fracture and can be powdered, but not readily. The crude wax melts at about 60° to a very viscous mass, which, on cooling, remains viscous for a long time, and from which an aqueous liquid separates. The sp.gr. of the wax after melting is 1·015 at 15°. It softens at 55°, and is only completely melted at 73°. It is soluble in benzene, chloroform, carbon disulphide, oil of turpentine, light petroleum, and boiling ether. Boiling alcohol dissolves it slowly, and the greater part separates on cooling. Cold alcohol keeps in solution a little over 5 p.c. of the wax. By means of boiling alcohol over 70 p.c. of white crystalline purified wax can be obtained, melting at 61°, insoluble in cold alcohol, but soluble in boiling alcohol. Greshoff and Sack (Rec. trav. chim. 1901, 20, 68), by analyses and saponification of the wax thus purified, obtained results suggesting that it is an ester $C_{30}H_{52}O_2$ of an alcohol $C_{17}H_{28}O$ (ficoceryl alcohol), with m.p. 198°, and of an acid $C_{13}H_{26}O_2$ (ficoceric acid), with a m.p. 57°, this ester is probably associated with some accessory substance; they also think the original wax contains some free ficoceryl alcohol.

Vogl (Lotos, pubd. at Prag, 1872, 22, 54) describes Sumatra wax or Getah Lahoe coming from the same tree. Kessel (Ber. 1878, 11, 2112) assigns formulæ to components of the wax which differ from the above.

Insect wax. This is also called *Chinese wax*, *Chinese tree wax*, *Vegetable spermaceti*, and sometimes, but incorrectly, *Japanese wax*; it must not be confused with Japan wax. It is the secretion of an insect *Coccus pela* (Westwood), *Coccus ceriferus* (Fabr.). The industry of its production is peculiar, in that the insects are bred for the purpose of producing eggs in one district, and these eggs are then transported to another district where the insects are reared to produce wax. The Chien-Chang valley in the prefecture of Ning Yuan Fu (Long. 102° 26′, Lat. 27° 54′) in the Sze Chuan province of China is the great breeding-ground of the wax insect; it is about 5000 ft. above sea-level. Here the insects are reared on the *Ligustrum lucidum* (Ait.) or large-leaved privet. In March, when the trees were seen by Mr. Hosie, he found numerous brown pea-shaped excrescences attached to the bark of the boughs and twigs. The larger of these were readily detachable, and when opened presented either a whity-brown pulpy mass or a crowd of minute animals like flour, whose movements were just perceptible to the naked eye. From 2 to 3 months later these had developed in each case into a swarm of brown creatures, each provided with six legs and a pair of antennæ; each of these was a wax insect. Two hundred miles to the north-east of the Chien-Chang valley, and separated from it by a series of mountain ranges, is the prefecture of Kia-ting-fu (Long. 104°, Lat. 29° 34′), also called Chia-ting-fu, containing the district of Omi and the valley of the Ya river, the headquarters of the wax-producing industry. The scales produced in the Chien-Chang valley are ready for removal by the end of April, and are then full of eggs; they are made up into paper packets, each weighing about 16 oz. Sixty of these packets make a load, and are conveyed by coolies from the Chien-Chang valley to the town of Hung Ya in the Kia-ting-fu prefecture for sale to the farmers. In May thousands of coolies are engaged in the traffic. They travel only at night, in order to avoid the high temperature of the day, which would tend to the rapid development of the insects and their escape from the scales. At the stopping places the packets are opened out in cool places; but in spite of this, each packet is found to have lost on an average an ounce in transit. A pound of scales laid down in Kia-ting-fu, in years of plenty, costs about half a crown; in bad years the price is doubled. In favourable years a pound of scales will produce 4–5 lbs. of wax. In the plain around Kia-ting-fu the plots of ground are thickly edged with stumps of *Fraxinus chinensis* (Roxb.), a species of ash varying from 3 or 4 to 12 ft. high, with numerous sprouts rising from their gnarled heads, and resembling at a distance pollard willows. On the arrival of the scales they are made up into small packets enclosed in a leaf of the wood-oil tree. The edges of the leaf are tied together with a rice straw, by which the packet is suspended close under the branches of this ash. A few rough holes are drilled in the leaf with a blunt needle, so that the insects may find their way through to the branches. On emerging from the scales the insects creep rapidly up to the leaves, among which they remain for a period of 13 days. They then descend to the branches, on the underside of which they take up their position, and commence to deposit the wax. This first appears as an under-coating on the sides of the boughs and twigs, and resembles quinine sulphate or a covering of snow. It gradually spreads over the whole branch, and attains, after 3 months, a thickness of about a quarter of an inch. After the lapse of 100 days the deposit is complete, the branches are lopped off, and as much of the wax as possible is removed by hand. This is placed in an iron pot of boiling water, and the wax on rising to the surface is skimmed off and placed in a round mould, whence it emerges as the insect wax of commerce. Where it is found impossible to remove the wax by hand, the twigs and branches are thrown into the pot, so that this wax is darker and inferior. The insects which have sunk to the bottom of the pot are placed in a bag and squeezed of the last drop of wax, and are then thrown to the pigs. Not only the *Fraxinus chinensis*, but also the *Ligustrum lucidum* is used in the final wax-producing stage of the industry. The wax is used for coating the exterior of animal and vegetable tallow candles, as it serves to hold in the more fusible tallow when the candle is burning; a little is also mixed with the tallow; it is employed to give a gloss to paper, for coating pills, and as a polish for furniture and jade-ware (Nature, 1891, 43, 291; Wilson, Chemi and Druggist, 1906, 68, 143).

Insect wax is white and crystalline, resembling spermaceti in appearance, but it i harder and more fibrous; it is brittle, and a 15° can be powdered. Its sp.gr. is 0·970 at 15 (0·926 at 15°, Gehe and Co., Zeitsch. anal. Chem 1895, 34, 765) and 0·809–0·811 at 98°–99°; m.p 80°–83°; saponification value 80–93; iodine valu 1·4. It is only very slightly soluble in alcoho and ether, but is readily soluble in naphtha from which it can be crystallised. Brodie (Phil. Trans. 1848, 159) saponified the wax by melting it with potash, and obtained an alcoho and an acid; the alcohol he named *cerotin*, and to it he assigned the formula $C_{27}H_{56}O$, it is now called *ceryl alcohol*; the acid he considered to be the same as the cerotic acid he had obtained from beeswax, to which he had assigned the formula $C_{27}H_{54}O_2$; the wax he regarded as ceryl cerotate, the ester of this alcohol and acid. Brodie's formulæ cannot be regarded as certain. Marie (J. Chem. Soc. 1897, 72, i. 318) proposes $C_{26}H_{52}O_2$ or $C_{25}H_{50}O_2$ for the cerotic acid of beeswax; and Henriques (*ibid.* 460) regards ceryl alcohol and cerotic acid from insect wax as $C_{28}H_{54}O$ and $C_{26}H_{52}O_2$, and it is stated that the identity of the cerotic acids from insect wax and from beeswax is not quite certain. Other substances besides ceryl cerotate are probably present.

Japan wax (*Japan tallow, Sumach wax*). This must not be confused with insect wax, which is sometimes called *Japanese wax*. Japan wax is one of the most important of the vegetable waxes, large quantities being exported from Japan: it is obtained from the berries of *Rhus succedanea* (Linn.), and of *R. vernicifera*, both of which grow in Japan and China; it is also said to be obtained from *R. sylvestris*, which grows in Japan. The wax is obtained in various ways. In *R. succedanea* the wax lies between the kernel and the outer skin of the berries; the meal obtained by crushing or grinding the berries is steamed and pressed, Perilla oil being often added in the course of the pressing in order to obtain a larger yield of the wax; such addition renders the wax softer and raises its iodine value. Another method is to boil the meal with water and remove the wax which rises to the surface. Occasionally the wax is obtained by extraction with solvents. The wax is purified by remelting, filtering, and bleaching in flakes, and is finally cast into cakes for export.

The wax is pale yellow and hard, with an even or conchoidal fracture; it becomes yellow or brown on keeping, and acquires a white powdery surface; it melts at 50°–56°, but if it has only recently solidified, the melting-point is considerably lower; it solidifies at about 41°, the temperature rising to 48° or 49° as it solidifies. It becomes transparent 10°–12° below its melting-point, which should be remembered in taking its melting-point. The sp.gr. is 0·975–0·993 at 15°; at 98°–99° it is 0·875–0·877, compared with water at 15·5°. Wax that has recently solidified has a lower density than that which has been kept for some time (Kleinstück, Chem. Zeit. 1890, 14, 1303). The saponification value is 214–237·5, and the iodine value is 4·2–15. The fatty acids obtained from it melt at 54°–62°. The unsaponifiable matter is 1·1–1·6 p.c. It dissolves in boiling alcohol, but nearly all separates on cooling. It is liable to adulteration with water and starch. It is used for making polishes and also for currying leather.

The wax consists chiefly of palmitin with some free palmitic acid. Its composition has been investigated by Eberhardt (Inaug. Diss. Strassburg, 1888), and by Geitel and van der Want (J. pr. Chem. 1900, [ii.] 61, 151); the latter found in the cakes they used acid values of 21·7–32·6, saponification values of 217·5–237·5, and iodine values 8·3–8·5. In one sample by saponification they obtained 5·96 p.c. of soluble and 90·62 p.c. of insoluble, fatty acids. By saponifying a large quantity they obtained glycerol and insoluble fatty acids, which contained a little oleic acid, and which were chiefly palmitic acid, and also contained an acid which they called *japanic acid*, melting at 117·7°–117·9° with a suggested formula $C_{20}H_{40}(CO_2H)_2$; they think it probable that this acid occurs in the wax as a mixed glyceride of palmitic and japanic acids. Schaal (Ber. 1907, 40, 4784) did not find the acid $C_{20}H_{40}(CO_2H)_2$ in the liberated fatty acids, but found small quantities of the acids $C_{19}H_{38}(CO_2H)_2$, $C_{18}H_{36}(CO_2H)_2$, and $C_{17}H_{34}(CO_2H)_2$, *v.* also JAPAN WAX, Vol. III. 187.

Mexican myrica wax (*Mexican myrtle wax*). This wax is obtained by the Indians in Mexico from the fruit of *Myrica jalapensis*, and is sold in Mexico city, where it is used for making candles. The tree is known locally as 'arbol de la cera,' and occurs in Vera Cruz, sometimes in dense thickets covering considerable areas. The wax forms a greenish-white layer on the outer surface of the fruit, and is obtained by boiling the fruit in water and skimming off the floating melted wax; it is refined by melting and straining. On examination it gave the following values, which resemble those of Cape berry wax: sp.gr. 0·8763 at 99°; m.p. 43·2°; acid value 4·07; saponification value 214·5; iodine value 2·38. It is considered that it would be suitable for making candles and soap (Olsson-Seffer, Bull. Imp. Inst. 1909, 7, 410).

Myrtle berry wax (*Myrtle wax*, *Laurel wax*, *Bayberry tallow*) is obtained from the wax myrtle, *Myrica cerifera* (Linn.), a shrub growing on peaty soil in North America, and common along the North Atlantic sea coast. The fruit is brown or blackish and the size of a pea; it secretes the wax and becomes covered with a snow-white crust, penetrated by brown or black points of the skin, so that the wax can only be got off as a powder and not in coherent pieces.

Wax is also got from other Myricaceæ, namely *M. caracasana* (Humb. and Bonpl.) in South America, especially in Columbia and Venezuela, and *M. aethiopica* (Linn.) in Abyssinia. *See* also *Cape berry wax* and *Mexican myrica wax* above.

To obtain the wax the berries are boiled with water, and the fatty mass that floats on the surface is skimmed off and poured into flat dishes; the yield of wax is from 20 to 25 p.c., and a bush yields from 10 to 15 kilos. of berries. The wax which comes from the United States has a deep green colour, probably due to chlorophyll; this colour is bleached to a grey-yellowish tint by exposure to light and air for several years, but the change extends only a few millimetres below the surface.

The statements as to its composition are not concordant. Smith and Wade (J. Amer. Chem. Soc. 1903, 25, 629), however, examined the wax, preparing it by extracting the berries with light petroleum, and concluded that it was mainly palmitin (glyceryl tripalmitate) with some lower glyceride and a small amount of free acid; they obtained pure palmitin by crystallising four times from light petroleum. The berries they used were picked in September, and the extraction and examination were made in November. The values they record are: sp.gr. 0·9806 at 22°/15·5°, and 0·878 at 99°/15·5°; refractive index at 80° 1·4363; acid value 30·7; saponification value 217; iodine value (Hübl) 3·9; Reichert-Meissl number 0·5. From these they inferred the absence of oleic and volatile acids. They also concluded that no stearin was present. The m.p. in this sample was 48°, as determined by Allen's method (vol. ii. pt. i. 34), and the solidifying-point was 45°; but it was found that the melting-point rises considerably on keeping the wax. A redetermination in March of the m.p. gave it as 52·5°, a rise of 4·5° in 4 months. A specimen of wax about 4 years old melted at 57° and solidified at 58·3°. Wax from berries obtained in August and extracted in March melted at 55·4°.

Some other observers have found the acid value to be only about 4. It is inferior to beeswax in ductility and plasticity; mixed with beeswax it can be employed for making candles; these are said to give a pleasant smell when extinguished. It could probably be used for soap making. Chittenden and Smith (Amer. Chem. J. 1884, 6, 217) employed this wax as a source for preparing pure palmitic acid.

Ocuba wax is obtained from the fruit of a shrub *Myristica ocuba* (Humb. and Bonp.), growing in the Para province of Brazil. It grows well in marshy places, and is found in abundance along the banks of the Amazon river. The fruit encloses a nut covered with a thick skin. The skin extracted by water gives a fine red colour (Ocuba red); after washing with water the nuts are thrown in heaps, crushed to a paste, and boiled, when the wax separates and floats on the surface. The crude wax resembles beeswax, and by purification can be obtained white and suitable for candle-making. 100 kilos. of the seeds give 20–22 kilos. of wax. The product is said to be a mixture of wax, fat, and resin, to melt at 40°, and to have a sp.gr. of 0·920 at 15°; it is only slightly soluble in cold alcohol, but is completely soluble in boiling alcohol and ether (Chem. Revue über die Fett- und Harz- Industrie, 1901, 8, 213).

Palm tree wax is the product of a palm tree *Ceroxylon andicolum* (Humb. and Bonpl.), which grows on the Andes in Columbia at altitudes of 7900–9700 ft.; it attains a height of 160 ft., and the trunk is coated with the wax, which gives it a white and marble-like appearance. The wax is obtained by cutting down the tree and scraping off the coating, which is then boiled with water; the wax is thus softened and floats on the surface, and impurities are removed. One tree is said to yield 25 lbs. The wax is made into balls and dried in the sun. Candles are made from it by the addition of a little tallow, and are sold in Carthago. That which is obtained from the Indians is yellowish-white, porous, and friable. When melted it is dark yellow, slightly translucent and fragile like resin. It is partly wax and partly resin, and melts at a temperature a little above that of boiling water; it becomes strongly electric by friction. It is readily soluble in hot alcohol; on cooling the solution becomes a white congealed mass. By using large quantities of alcohol and allowing the solution to cool the waxy part separates and the more soluble resin remains in solution; by repeating this operation several times the wax can be separated from the resin and from a small amount of a bitter substance. Ether also dissolves it, and by evaporation feathery crystals can be obtained. The purified wax melts below the temperature of boiling water, and then resembles beeswax, whilst the resinous matter melts above this temperature (Boussingault, Ann. Chim. Phys. 1825, 29, 330; 1835, 59, 19; Seemann, Pop. Hist. of the Palms, 1856, 222).

Bonastre (J. Pharm. Chim. 1828, 14, 349) obtained purified wax by repeated extractions with cold alcohol, and then dissolving the residue in boiling alcohol and filtering. When cold the solution became thick and opaque, like an aqueous starch solution; on standing for some months crystals appeared. On removing the alcohol white silky crystals were obtained; when dried and ground in a mortar it gave luminous sparks. He named this purified wax *ceroxyline* or *cerosiline*. Lewy (Ann. Chim. Phys. 1845, [iii] 13, 447) found that the wax purified from the resin melted at 72°, and contained carbon 80·73 p.c., and hydrogen 13·30 p.c. Teschemacher (Mem. and Procs. Chem. Soc. 1845, 25) also describes this wax.

Peat wax. Waxy substances are obtained when peat is extracted with suitable solvents. By means of benzene or toluene from 1 to 8 parts of crude wax have been obtained from 100 parts of the dry material of samples from different sources. This crude wax was found to contain sulphur, usually amounting to less than 1 p.c. of the wax, but in one case reaching 10·5 p.c. The crude wax consisted of some resinous matter, but principally of a mixture of ester and free acid. The acid or acids obtained by the saponification of the crude wax corresponded in composition to a fatty acid containing about 22 carbon atoms; the alcohols thus obtained appeared to contain about the same number. No trace of glycerides was found (Kraemer and Spilker, Ber. 1902, 35, 1212). A process was patented in 1903 by Bouchaud-Praceiq (Fr. Pat. 338736) for extracting peat, lignite, &c., with alcohol or ethyl esters, &c., and recovering the wax from the solvent. The wax is said to be hard and to resemble beeswax, and to have a higher melting-point and a sp.gr. above 1·000 (J. Soc. Chem. Ind. 1904, 23, 710).

Zaloziecki and Hausmann (Zeitsch. angew. Chem. 1907, 20, 1141), by extracting peat with alcohol, obtained a dark yellow or brown waxy substance, but the yield was only 10 grms. from some kilograms. It had no sharp melting-point, melting between 80° and 96°; it dissolved very easily in amyl alcohol, and less readily in ethyl and methyl alcohols. In ethyl ether or benzene it dissolved only partially, giving a dark green liquid and leaving a brown insoluble residue. By saponifying the substance soluble in ethyl ether an alcohol was obtained, melting between 124° and 130°, and having a composition and molecular weight corresponding to $C_{20}H_{40}O_4$, and also an acid which began to soften at 145° and melted at 184°, having a composition and molecular weight corresponding to $C_{18}H_{25}O_5$. The part insoluble in ether gave on saponification an alcohol having the same melting-point, composition and molecular weight as the other alcohol, but differing a little in its behaviour, and also an acid which had not melted when 260° was reached, and which had a composition and molecular weight corresponding to $C_{21}H_{25}O_7$. Small quantities of other substances appeared also to be present in the wax, and the above substances are very possibly mixtures.

Pisang wax. This wax occurs as an excretion on the leaves of a species of *Musa*, which grows wild in Java, especially in the uncultivated regions of Tjilatjap and Koeningan. *Pisang* is the Malay name for the banana. The natives obtain the wax by scraping the leaves, throwing the scrapings into boiling water, and then collecting the melted wax. It is said that one stem bears on the average seven leaves (a leaf may be as much as 6 ft. in length), and that 100 leaves yield ½ kilo. of wax. The cakes of wax are white, cream, or slightly greenish in colour, and slightly transparent; the wax is hard with a coarsely granular or crystalline fracture and is very friable. It has been examined by Greshoff and Sack (Rec. trav. chim. 1901, 20, 65), who record the following: sp.gr. 0·963–0·970 at 15°; m.p. 79°–81°; acid value 2–3; it is very hard to saponify, and the saponification value found was 109. Boiling alcohol dissolves very little (about 1 p.c.), and on cooling only retains 0·2 p.c. It is easily soluble in boiling oil of turpentine, amyl alcohol, or carbon disulphide. At 15° petroleum, ether, acetone, and oil of turpentine retain 1 p.c. or less; chloroform and carbon disulphide retain less than 2 p.c. On the basis of ultimate analyses of the wax, freed from the part soluble in boiling alcohol, and of the acid and alcohol obtained by saponification, the authors propose provisionally the formula $C_{37}H_{74}O_2$ for the wax, regarding it as an ester formed from $C_{24}H_{48}O_2$ *pisangceric acid*, and $C_{13}H_{28}O$ *pisangceryl alcohol*. The acid melts at 71°, and the alcohol at 78°.

Raphia wax. The raphia palm, *Raphia pedunculata* (Beauv.) or *Ruffia*, which grows in Madagascar, furnishes the fibrous material used by gardeners and known as 'bass'; this is the epidermis of the upper side of the palm leaf. The dull under surface is coated with a whitish layer or bloom, which can be easily rubbed off. After the bass is removed large quantities of the residues are available as a source of the wax. They are spread out to dry on cloths in the open air, but must be sheltered from the wind as the light waxy matter is easily blown away. After drying for 2–4 days a white coating is apparent on the under surfaces of the leaves; this is detached as a powder by shaking or rubbing the leaves between the hands. The powder is collected, freed from foreign matter by sifting, and then put into boiling water when the wax melts and floats on the surface, and earthy impurities settle to the bottom. The melted wax is separated and allowed to solidify. It is yellow to dark brown in colour, and rather harder and more brittle than beeswax. In an experimental trial it was found that ten leaves of medium size (3½–4½ metres in length) weighed 104·5 kilos. and yielded 0·75 p.c. of wax; the yield in practice, however, would be less than this.

Raphia wax in its physical properties resembles carnaüba wax but differs chemically; it seems likely to be applicable to the manufacture of candles, polishes, &c., if it can be produced at a sufficiently low cost.

Two specimens were found to have the following properties: m.p. 82°, 83°; sp.gr. 0·836, 0·832 at 99°/15·5°; acid value 4·9, 6·5; saponification value 51·3, 50·3; iodine value 7·7, 10·7 (Bull. Imp. Inst. 1908, 6, 380). It is only slightly soluble in alcohol, ether, acetone, chloroform, light petroleum, and carbon disulphide. It dissolves, but not completely, in boiling alcohol, and separates on cooling. It appears to be mostly composed of an alcohol or mixture of alcohols having a composition corresponding to $C_{20}H_{42}O$, but differing from arachic alcohol (Compt. rend. 1905, 141, 1251; 1907, 144, 594).

Spermaceti occurs in special cavities in the head of the sperm whale or cachalot, *Physeter macrocephalus* (Linn.), and also in the blubber; it is held in solution by the sperm oil at the temperature of the whale's body. It also occurs in the bottle-nose whale *Balaena rostrata*, and in some other cetaceans, but not in the oil of the whalebone whales. The spermaceti from *Balaena rostrata* has a slightly higher melting-point than that from the sperm whale. The great bulk of the head of the sperm whale consists of dense cellular tissue infiltrated with spermaceti, this is surmounted by the 'case' which holds nearly a ton of very fine oil and spermaceti known as 'head matter.' When removed this head matter is full of spermaceti crystals. The blubber surrounds the whole body in a layer about 18 ins. thick; it is 'tried down,' that is heated to separate the oil from the tissue; on cooling the oil deposits thick scales of spermaceti and becomes semi-solid. The 'trying down' is sometimes done on the ship and sometimes at the factories. At the latter the semi-solid mass undergoes several filtrations and pressings to separate the oil from the spermaceti, which is melted and cast into moulds once or twice during the series of pressings. Finally, the wax is warmed and agitated with a little caustic potash solution to remove the last traces of colour and to neutralise traces of acid, and is cast into blocks forming an almost blue-white glistening semi-crystalline solid (Field, Soc. Arts. Cantor Lectures, 1883). It is said that for some purposes it is best not to free it entirely from the sperm oil.

The sp.gr. at ordinary temperatures is about 0·945, but values as divergent as 0·905 and 0·960 have been given, owing probably to irregularities caused by the crystalline structure. The sp.gr. of melted spermaceti at 98°–99° is from 0·808 to 0·816 as compared with water at 15° (Kebler, Amer. J. Pharm. 1897, 69, 104). The m.p. is from 41° to 49°, but by repeated purifications it reaches 53·5°. The acid value is from 0 to 1·8; saponification value from 120·6 to 134·6; the iodine value of highly purified spermaceti is 0, but values up to 9·3 (by Wijs' method) have been found, caused, no doubt, by the presence of sperm oil (Dunlop, J. Soc. Chem. Ind. 1908, 27, 63). It is insoluble in water; cold alcohol dissolves little except the adhering oil, it is soluble in boiling alcohol, ether, chloroform, carbon disulphide; it separates in a crystalline form from its solution in hot alcohol or ether.

Spermaceti is mainly composed of cetyl palmitate $(C_{16}H_{33})C_{16}H_{31}O_2$. It was examined by Chevreul in 1814, and the purified substance was named by him *cétine*; in 1818 he described the alcohol obtained by its saponification (now known as *cetyl alcohol*) under the name *ethal*, formed from the first syllables of ether and alcohol (Recherches, Chim. sur les Corps Gras. 1889, 148). The acid with which the cetyl alcohol $C_{16}H_{33}OH$ is combined was found later to be palmitic acid. Although spermaceti has a crystalline appearance, it contains compounds other than cetyl palmitate. Heintz (Pogg. Ann. 1854, 92, 609, 93, 536) believes that it yields on saponification stearic, palmitic, myristic, and lauric acids, and the alcohols $C_{18}H_{38}O$, $C_{16}H_{34}O$, $C_{14}H_{30}O$, and $C_{12}H_{26}O$; he named the first, third, and fourth of these *stethal*, *methal*, and *lethal* in analogy to Chevreul's *ethal*. These very probably exist in the spermaceti as esters of the corresponding acids. He also found another liquid substance in the products of saponification.

Spermaceti is used for making candles which burn brightly and in pharmacy for making ointments. For candle-making the addition of a few per cent. of beeswax or paraffin is advantageous to remove the brittleness of the spermaceti. Sperm candles of prescribed composition and properties were formerly used as the standard for measuring the illuminating power of different lights (Young, J. Soc. Chem. Ind. 1891, 10, 185; Met. Gas Referees, *ibid.* 1894, 13, 65); but now a pentane lamp is used, representing ten standard candles.

Sugar cane wax. A waxy substance is produced by the sugar cane, and is noticeable on the rind of some varieties, especially near the nodes; it is most abundant on the violet cane. It was first described by Avequin (Ann. Chim. Phys. 1840, [ii.] 75, 218), who named it *cérosie*. Cold alcohol removes some colouring matter, chlorophyll probably, but does not dissolve the wax. The purified wax can be obtained by removing the portion soluble in cold alcohol, then dissolving in boiling alcohol, cooling, pressing, driving off the alcohol, and melting. It is dull yellow, hard, and can be powdered; it is insoluble in water, cold alcohol and cold ether; hot ether dissolves it to some slight extent, and deposits it on cooling in small crystalline grains; boiling alcohol dissolves it completely, and the solution on cooling becomes semi-solid, just as does an alcoholic soap solution. It melts at 82° and solidifies at 80°, and its sp.gr. is 0·961 at 10°. When made into a taper it burns with a fine white flame like wax or spermaceti.

Analyses of the wax were made by Dumas (*ibid.* 222) and Lewy (*ibid.* 1845, [iii.] 13, 451) who assigned formulæ to it on the supposition that it was a single compound, but from Wijnberg's experiments (Het Rietwas en de Mogelijkheid zijner Technische Winning, 1909; J. Soc. Chem. Ind. 1909, 28, 991) the wax appears to contain about 45 p.c. of myricyl alcohol $C_{30}H_{62}O$, and also a substance with a composition corresponding to $C_{33}H_{68}O$, which is neither an ester nor a primary alcohol, since it yields no hydrogen when heated with soda lime. Prinsen Geerligs (Arch. v. d. Java-Suikerindustrie, 1893, 1, 67) also examined the wax.

In the manufacture of cane sugar the juice is purified by treatment with lime and heating; the resulting muddy precipitate is filtered off and forms a waste product. Wijnberg proposes to extract the wax from this by the use of benzine or other solvents and utilise it (Fr. Pat. 397843, 1908). He finds that the extract from fresh mud contains a large proportion of fatty matters besides the wax, but that in mud which has been kept for some time the fatty matters undergo a kind of fermentation, and are decomposed and a product is obtained approximating more closely to the wax got by scraping the cane. It is stated that extraction of the wax has been undertaken in Java. The subject is treated of very fully in Wijnberg's book mentioned above. H. H. R.

WEED KILLERS. The best weed killer for the purpose of the agriculturist is generally the hoe in some form or other, aided by the sun and wind. To permit of the ready discrimination, by mechanical means, between the crop and the accompanying weeds is one of the most important advantages of regular drilling or planting. It is only in a few cases that the farmer can derive much advantage from the application of chemical methods of destroying weeds, since, as a rule, any means which will destroy weeds, will render the soil, for a time at least, unfitted for the growth of any plant.

For destroying *all* vegetation, *e.g.* for keeping garden paths free from weeds, any general plant poison may be used. Of these there are many; indeed any soluble salt, applied in strong solution, will kill plants by producing plasmolysis. In practice, strong solutions of common salt, 10 p.c., *i.e.* 1 lb. per gallon; dilute sulphuric acid (1 part in 25 to 30 of water); dilute solution of phenol (about 1 oz. commercial carbolic acid to a gallon of water); of sodium arsenite (about 1·5 p.c. solution); or of calcium sulphide (made by boiling 1 part of sulphur with 50 parts of water and 10 parts of quicklime) are often used, the liquid being simply applied to the surface of the walks from a watering pot, which should be well painted on the inside. Sulphides, thiocyanates, and sulphites act as effective plant poisons, and to their presence the poisonous action of fresh 'gas lime' is largely due. Many metallic salts act as plant poisons, even in excessively dilute solution. According to Coupin (Compt. rend. 1901, 645) the weakest solutions of the various salts which had an injurious effect upon the growth of the roots of the seedlings of wheat, contained 1 part of the anhydrous salt and the following parts of distilled water:—

Copper sulphate . .	700,000,000
Mercuric chloride . .	30,000,000
Cadmium chloride .	10,000,000
Silver nitrate . .	1,000,000
Zinc sulphate . .	40,000
Lithium chloride . .	12,000
Calcium iodide . .	10,000
Barium nitrate . .	4,200
Borax	1,000
Manganese chloride .	1,000
Calcium bromide . .	400
Calcium chloride . .	260

The extreme dilution of the copper sulphate which can produce a poisonous effect, *when applied in solution to the roots*, is remarkable. In the presence of soil, however, many of these substances, including copper sulphate, are converted into insoluble and harmless compounds.

But the use of these plant poisons in agricultural practice is limited, owing to the difficulty of restricting their action to the weeds. In some countries, where a particular weed has become a scourge, recourse to these drastic measures is sometimes made, *e.g.* prickly pear in Cape Colony has been destroyed in many districts by the use of sodium arsenite, or of solutions of arsenical sheep dips, 1 or 2 p.c. solution of the former being sprayed over the uprooted trees, which then die and can afterwards be burnt.

Of more importance to the farmer is the *differential* or *selective* poisoning of weeds, by the use of solutions which, while destroying certain weeds, produce no injurious effect upon the crop itself. The best known of such methods is in the destruction of charlock or wild mustard (*Sinapis arvensis* [Linn.] or *Brassica Sinapistrum* [Boiss.]). The method, due to an accidental observation by Girard in France, in 1897, is to spray the barley or oat field infested with the charlock in the spring, when the charlock plants are about 2 or 3 ins. high, with from 40 to 70 gallons per acre of a 3 p.c. solution of crystallised copper sulphate, best on a still, dry, dull day. Unless rain soon follows the spraying, in which case the result is spoiled, it will be found that the charlock plants quickly blacken and die, while the barley or oats and clover (if that be also present) are uninjured. In addition to charlock, known in various districts as 'ketlock,' 'wild mustard,' 'yellow flower,' and in Ireland as 'preshaugh,' other cruciferous weeds, of which 'runches' (*Raphanus raphanistrum*) is the most important, can be killed by the same treatment. Ferrous sulphate in 10 or 12 p.c. solution may be substituted for the copper sulphate, but according to experience in Ireland (Leaflet No 6. Dept. of Agric. and Tech. Instruction for Ireland. 1901) is not so efficient. Cereals, clovers (and most other *leguminosæ*) are uninjured by the treatment, but docks and thistles, although not usually killed, are seriously checked in growth.

Various explanations of this differential action of copper and iron sulphate solutions have been offered. Girard ascribed it to the solution being retained by the rough and more or less horizontal leaves of the charlock, while the smooth erect leaves of the cereals would permit of the solution running off. Against this is the fact that other plants with horizontal leaves, *e.g.* clovers, suffer little damage. Another possible explanation is that interaction between the metal of the copper or iron sulphate and the sulphur compounds which are characteristic of the *cruciferæ*, may take place and lead to the destruction of the plant.

A third and probable theory is that the cell walls of the leaves of charlock are thinner or weaker than those of cereals, and more readily permit of plasmolysis being set up, when they are brought into contact with saline solutions applied to the exterior of the leaves. This view receives some support from the fact, observed by Heinrich (Jahresb. fur Agricultur-Chemie, 1901, 351), that 15 or 20 p.c. solutions of sodium nitrate, ammonium sulphate, or potassium chloride—substances which cannot exert any chemical toxic effect—are also effective in destroying charlock. Moreover, the importance of a dull, still, dry day for the spraying, which is always shown in field trials, is in accordance with this explanation, for under such conditions, the droplets of the solution, deposited on the leaves of the plant, would retain their original concentration for a longer period than on windy or sunny days when evaporation would be hastened.

The experience of the Irish Department of Agriculture is that from 50 to 70 gallons per acre of a 3 p.c. solution of copper sulphate, under favourable conditions of weather, is the most effective spray for destroying charlock in cereal crops, and that even when the weed has come into flower, it can be successfully destroyed by this treatment, whilst the cereals and clover are uninjured.

A certain amount of indirect 'weed' killing can be achieved by suitable manuring; thus the growth of grasses is favoured at the expense of admixed leguminous plants, by repeated applications of nitrogenous manures, whilst the opposite effect is produced by application of calcareous, phosphatic, and potash manures with avoidance of nitrogenous ones. But this method is of limited application, and is rarely of service to the farmer. It may, however, be used in the adjustment of the relative proportions of grasses and clovers in a lawn. But for the destruction of the more important and troublesome weeds of the farm and garden reliance has chiefly to be placed upon the mechanical methods of cultivating the soil at the most suitable season. H. I.

WEISSENFELS LIGNITE RESINS *v.* Resins.

WEISSGILTIGERZ or **WEISSGÜLTIGERZ** *v.* Freibergite.

WELD is the dried herbaceous plant known as the *Roseda luteola* formerly cultivated to a considerable extent in France, Germany, and Austria. Its cultivation in this country has nearly ceased, because not only is the quantity of colouring matter present very small, but the carriage of the plant, owing to its bulky nature, is extremely expensive. A special interest, however, attaches to weld, for it is said to be the oldest European dyestuff known, and was used by the Gauls and other nations dwelling north of the Alps in the time of Julius Cæsar.

The plant attains a height of about 3 feet, is pale brown in colour, and is sold in sheaves like straw. The colouring matter is disseminated throughout the entire plant, but the greater quantity occurs in the upper extremity and the seeds.

Luteolin, the main colouring matter of weld, was examined by Chevreul (J. Chim. Med. 6, 157; Annalen, 82, 53), who obtained it in a crude condition; its isolation in a state of chemical purity was first achieved by Moldenhauer (Annalen, 100, 180), who assigned to it the formula $C_{20}H_{14}O_6$. It was subsequently investigated by Schützenberger and Paraf (Bull. Soc. chim. 1861, [i.] 18), who proposed the formula $C_{12}H_8O_5$ and purified it in a somewhat novel manner which is worthy of mention. Weld was exhausted with alcohol, the extract evaporated, and treated with water, which threw down a dirty greenish precipitate. This was collected, introduced with a little water into a sealed tube and heated to 250°. On cooling the sides of the tube were found to be coated with golden-yellow needles of luteolin, and the impurities had collected at the bottom of the tube to form a resinous cake.

Hlaziwetz suggested that luteolin had the formula $C_{15}H_{10}O_6$, and was isomeric with the *paradiscetin*, which he obtained during the fusion of quercetin with alkali (Annalen, 112, 107).

For the preparation of luteolin in quantity Perkin (Chem. Soc. Trans. 1896, 69, 206, 799) employs weld extract.

300 grms. of the extract dissolved in 3 litres of water is treated with 100 c.c. of hydrochloric acid (33 p.c.), and the mixture is digested at the boiling temperature for some hours. A quantity of a black resinous substance separates, which is collected while hot, and the filtrate, which contains the colouring matter, is allowed to stand for 12 hours. A brown precipitate of impure luteolin is slowly deposited, and is collected, washed, and dissolved in a little hot alcohol. On pouring this solution into ether, the main bulk of the impurity is precipitated, and the ethereal liquid on evaporation yields a yellow residue, which is crystallised from dilute alcohol. The product in addition to luteolin contains apigenin (Chem. Soc. Trans. 1900, 77, 1315), and the latter can only be removed with certainty by the following method. The mixture dissolved in boiling glacial acetic acid is treated with a few drops of strong hydrochloric acid; this causes the almost immediate separation of luteolin as hydrochloride, whereas the apigenin remains in solution. The hydrochloride is collected, decomposed by water, and the luteolin crystallised from dilute alcohol.

Luteolin $C_{15}H_{10}O_6$ crystallises in yellow needles or leaflets, m.p. 327°–329° (Perkin), 327° (Kostanecki, Różycki and Tambor, Ber. 1900, 33, 3410), soluble in alkaline solutions with a yellow coloration. With alcoholic lead acetate it gives a bright yellow precipitate, and with alcoholic ferric chloride a green solution.

Luteolin sulphate $C_{15}H_{10}O_6{\cdot}H_2SO_4$, orange-red needles; *luteolin hydriodide* $C_{15}H_{10}O_6{\cdot}HI$, orange prisms; *luteolin hydrobromide*

$$C_{15}H_{10}O_6{\cdot}HBr,H_2O,$$

ochre needles; and *luteolin hydrochloride*

$$C_{15}H_{10}O_6{\cdot}HCl,H_2O$$

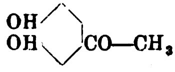
(Perkin, *l.c.*) are readily prepared by the action of the acids on luteolin in the presence of boiling acetic acid. By treatment with water these compounds are quantitatively decomposed into luteolin and the acid.

Monopotassium luteolin $C_{15}H_9O_6K$, fine yellow needles, from luteolin by means of alcoholic potassium acetate, is decomposed by boiling water with separation of luteolin. The *sodium* compound $C_{30}H_{19}O_{12}Na$ behaves similarly.

Tetra-acetyl luteolin $C_{15}H_6O_6(C_2H_3O)_4$, Perkin, also Herzig (Ber. 1896, 29, 1013), colourless needles, melts at 221°–223° (P.), 225°–227° (H.). *Tetrabenzoyl luteolin* $C_{15}H_6O_6(C_7H_5O)_4$, colourless needles, melts at 200°–201° (P.).

Dibromluteolin $C_{15}H_8Br_2O_6$, yellow needles, melts at 305°.

By the action of nitric acid on luteolin Rochleder (Zeitsch. Chem. 1886, 602) obtained oxalic acid, and with fused alkali *protocatechuic acid* and *phloroglucinol*. Digested with boiling 50 p.c. potassium hydroxide solution, phloroglucinol and *acetylcatechol* are produced (Perkin and Horsfall, Chem. Soc. Trans. 1900, 77, 1322).



When methylated in the usual manner luteolin behaves somewhat peculiarly, for it yields, in addition to luteolin trimethyl ether, also methyl luteolin trimethyl ether (P. and H.).

Luteolin trimethyl ether $C_{15}H_7O_3(OCH_3)_3$, lemon-yellow needles, m.p. 161°–163°, forms a *monoacetyl* derivative $C_{15}H_6O_3(C_2H_3O)(OCH_3)_3$, colourless prisms, m.p. 156°–158°, and with alcoholic potash gives a bright yellow crystalline salt, which is decomposed by water.

On hydrolysis with alcoholic potash at 170° the trimethyl ether gives *veratric acid*, and *phloroglucinol monomethyl ether*, which was isolated in the form of *disazobenzene phloroglucinol monomethyl ether*, orange needles, m.p. 251°–252°.

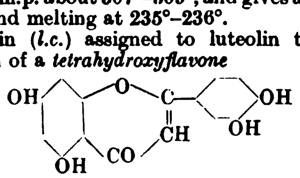
Methyl luteolin trimethyl ether

$$C_{16}H_9O_3(OCH_3)_3,$$

melts at 191°–192°, and the *monacetyl derivative* $C_{16}H_8O_3(OCH_3)_3(C_2H_3O)$ at 175°–176°. By means of alcoholic potash *veratric acid* and *methyl phloroglucinol methyl ether* (identified as *disazobenzene methyl phloroglucinol monomethyl ether*, orange-red needles, m.p. 198°–201°) are produced.

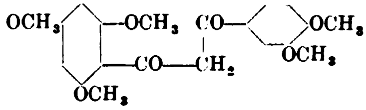
By digestion with boiling hydriodic acid *methyl luteolin* $C_{16}H_{12}O_6$, yellow leaflets, is formed, m.p. about 307°–309°, and gives an acetyl compound melting at 235°–236°.

Perkin (*l.c.*) assigned to luteolin the constitution of a *tetrahydroxyflavone*



and the more recent synthesis of this colouring matter by v. Kostanecki, Różycki and Tambor (*l.c.*) has indicated that this formula is correct.

When *phloracetophenone trimethyl ether* is condensed with *ethyl veratrate* it gives 2 : 4 : 6 : 3′ : 4′ *pentamethoxybenzoylacetophenone*,



and this by long digestion with boiling hydriodic acid (sp.gr. 1·96) is converted into luteolin.

When air is aspirated through alkaline solutions of luteolin (and also those of chrysin and apigenin), oxidation does not occur. This property, according to Perkin (*l.c.*), distinguishes the colouring matters of the flavone from those of the flavonol class, which are readily oxidised by this treatment.

It has already been stated that weld contains a second colouring matter *Apigenin*, *v.* PARSLEY.

Dyeing properties of weld. The importance of weld as a dyestuff in silk and wool dyeing has greatly diminished in consequence of its low colouring power compared with quercitron bark, flavin, and old fustic. This in one respect is unfortunate, because of all the natural yellow colouring matters, it yields the purest and fastest shades. In conjunction with aluminium and tin mordants it gives very bright pure lemon-yellow colours, and these do not change to an olive or reddish tint as is the case with other vegetable yellows. With chromium and iron mordants weld gives yellowish and greenish olives respectively. For yellow, wool and silk are mordanted with alum and tartar in the usual manner and dyed subsequently in a decoction of weld with the addition of chalk to the dye-bath. Weld alumina yellow is to some extent still employed for certain army cloths and braid in this country. For silk dyeing, weld extract is manufactured in small quantity, and is used for the production of yellow and olive colours.

A. G. P.

WELDING (*Soude*, Fr.; *Schweissen*, Ger.) is the joining of two pieces of metal under the hammer at a sufficiently high temperature.

WESELSKY'S DYES *v.* OXAZINE COLOURING MATTERS.

WESTFALITES. Explosives consisting of mixtures of ammonium nitrate and resin, with or without potassium nitrate, *v.* EXPLOSIVES.

WETTER DYNAMITE, WETTEREN POWDER, *v.* EXPLOSIVES.

WHALE OIL is obtained from the blubber of various species of the genus *Balaena*, viz. *Balaena mysticetus*, Greenland or 'right' whale (northern whale oil); *Balaena australis* (southern whale oil); *Balaenoptera longimana*, *Balaenoptera musculus* (common rorqual, the largest of all known animals), *Balaenoptera borealis* (northern or Rudolphi's rorqual; finback oil, finner-whale oil, humpback oil); *Neobalaena marginata* (Australian whale); *Rhachianectes glauca*, Cope (Japan). Other cetaceans, the zoological species of which have not been determined yet, or which are identical with the foregoing species, are known as bowhead whale, Californian grey whale, orca or killer whale, beluga or white whale; these are chiefly caught by American whalers in the Northern Pacific. The northern whale oil is the 'train oil' of commerce proper; but this name has become a generic name, and has been extended to all other 'blubber oils' included in this group and even to fish oils (*see* OILS, FIXED, AND FATS).

The blubber of whales caught in the northern seas of Europe was, in the early days of the whaling industry, 'tried' on board the whalers; but in consequence of the low yield, and also of the low quality of oil thus obtained, the whales are now brought into the 'trying' stations situated in Finmarken, on the Lofotes, Faro, Shetland, Hebrides, and in Iceland.

To a large extent the American whalers still 'try' the blubber on board ship and deliver the crude oil into the refineries of New Bedford, Mass., on the east coast, and of San Francisco on the west coast. In British Columbia the most modern methods (*see* below) are now in vogue.

During recent years a very extensive whale oil industry has sprung up in the whaling grounds adjacent to the South African coast, especially to that of Natal. The whale, killed by a gun shot, is blown up with air so as to float the carcase, which is brought immediately into the trying stations, when the whale is hoisted on to a working platform where the blubber is stripped clean from flesh, and care is taken to leave as little flesh as possible on the blubber. The latter is then cut into strips, which are thrown into chopping machines, whence the comminuted mass is immediately delivered into melting-pans, and 'boiled' with steam. Five different qualities of whale oil are produced. The best quality is the oil which first runs off the blubber at the lowest temperature, known in commerce as 'Whale Oil No. 0'; it is of a pale-yellow colour, and has but a faintly fishy smell. This oil contains a very small quantity of free fatty acids. The best brands are 'water-white,' and are free from volatile fatty acids. On further boiling, the second quality—'Whale Oil No. 1'—runs off; it is a little darker in colour, although still pale yellow. Its fishy smell is more pronounced than the oil of the first running.

These two qualities of oil are stored in large vessels, whereby they become clarified whilst depositing 'stearine,' which is filtered off, pressed in hydraulic presses, and sold as 'whale tallow,' 'whale stearine,' for soap-making.

The residual mass in the boiling pans, together with the flesh of the whale, is cut up into strips or fairly large lumps, and is 'tried down' in a digester under a pressure of 40–50 lbs. The oil classed as 'No. 2 oil' is thus obtained. This oil has a brown colour and a strongly developed fishy smell; its proportion of free fatty acids is considerably higher than in 'oil No. 1.' In some stations 'whale oil No. 2' is made from the blubber residues only, and does not contain any oil from the flesh. Hence it represents a superior article to the 'No. 2 oil.'

The bones are worked up in the same manner, and yield a still inferior quality of oil. Such oil ('whale oil No. 3') is darker still, has a more strongly developed odour, and a high percentage of free fatty acids. 'Whale bone oil' of commerce is, however, not exclusively made from the bones, except in those cases where the product is sold under guarantee as 'bone oil.'

All these operations are carried out with the greatest rapidity and precision simulating the routine of the Chicago packing houses which have served as a prototype to the arrangement of a modern whaling station.

In the old whaling stations where the carcase cannot be handled so expeditiously, the oil remains for a longer or shorter time in contact with the flesh, which rapidly undergoes putrefactive changes. The oil suffers in consequence and becomes dark, and is more objectionable as regards smell and free fatty acids than the preceding qualities. This oil is known in the trade as 'carcase oil,' 'whale oil No. 4.'

The residue remaining after the removal of the oil is worked up for manure, 'whale guano.'

This process is carried out in Newfoundland (at Balena) Pacific coast, and South Africa, where the Government has established several new plants. The carcasses of the whale are there completely used up in the manufacture of oil, 'stearine,' bone meal or bones, and other articles of commerce.

If the whale is landed in a perfectly fresh state, cattle meat can be prepared from the fresh meat, as is being done in Iceland and in the Faro Islands, and in South Africa. Some fresh meat is also consumed by the inhabitants locally (Iceland and Faro Islands).

The 'right whale' oil is of better quality than the 'southern whale' oil. The 'finner whale' oil is of still lower quality. Hence the finner whale was formerly neglected by the whalers, but at present even this kind of whale is eagerly pursued by them along the coasts of Norway and Newfoundland, as also to a smaller extent on the Asiatic coast of Russia, and the coast of Japan. For the chemical characteristics of whale oil, *see* OILS, FIXED, AND FATS.

The chemical composition of the whale oil fatty acids has not yet been established satisfactorily. The deposited 'stearine' consists to a large extent of palmitin. The iodine value of a sample of pressed cake examined in the author's laboratory was 37·9. Volatile fatty acids are absent; the high Reichert values recorded by earlier observers are undoubtedly due to the specimens examined having been highly rancid. The liquid fatty acids are characterised by the occurrence of clupanodonic acid, of which about 10 p.c. can be isolated from whale oil in the form of its octobromide.

Whale oil is not infrequently adulterated with rosin oil, the detection of which is simple. More difficult is the detection of admixed seal oil, on account of the great similarity of the two oils; at present this is practically impossible by chemical means; taste alone permits the recognition of seal oil.

The 'water-white' and 'pale' brands of whale oil are used as burning oil, and very extensively in soap-making. The lower qualities are employed for leather-dressing.

Whale oil is also used as a batching oil for jute, for tempering steel, and as a lubricant for screw-cutting machines. J. L.

WHEEL ORE *v.* BOURNONITE.

WHETSLATES *v.* WHETSTONE.

WHETSTONE. Some of the finest whetstones for sharpening edged tools, such as the 'Arkansas stones,' are made from *novaculite*, a rock so called from *novacula*, a razor. The sharpening quality is said to be due to the presence of disseminated crystalline silica, or, in some varieties, to minute crystals of garnet or rutile. The rock is so hard that it has to be cut with diamond dust. Some of the pure white novaculite seems to be a silicious deposit from hot springs, whilst other varieties are altered schistose rocks of fine grain. The so-called 'Hindostan whetstone' is worked in the State of Indiana, whilst the stone known as 'chocolate whetstone' is a mica-schist from New Hampshire. The famous 'German razor hones' are formed of a fine-grained argillaceous rock, occurring in slate near Ratisbon. The Scotch 'snake stone' or 'Water-of-Ayr stone' is used for rubbing down the surfaces of other stones and of copper-plates. 'Tam o' Shanter hones' are employed as ordinary whetstones. Coarse whetstones, used chiefly for scythes, have been worked for many years near Blackdown in Devonshire, and are known as 'Devonshire batts.' They are made from silicious concretions embedded in sand, probably of Upper Greensand age. Somewhat similar scythe stones have been worked at Penzlewood near Stourton in Wiltshire.

(H. B. Woodward, Geol. Eng. 1887; Renard, Mem. Ac. R. Belgique; Rep. Geol. Surv. Arkansas, 1890, vol. 3, Whetsones, by L. S. Griswold; G. P. Merrill, The Non-Metallic Minerals, 2nd ed. New York, 1910); *v.* OILSTONE.

WHISKEY. The term 'whiskey,' applied to the national beverage of Scotland and Ireland, only came into common use in the latter part of the eighteenth century, and is derived from the Celtic 'uisque-beatha' or 'usquebaugh,' meaning 'water of life,' no doubt in reference to its stimulating properties. A similar signification is seen in the terms applied to strong alcoholic liquors in other countries, as 'aqua vitæ,' and 'eau de vie.' Burns employs the three terms 'aqua vitæ,' 'usequbæ,' and 'whiskey' synonymously.

The introduction of the manufacture of alcohol into Europe is, as the word suggests, due to the Arabs, but in the grape-growing countries of the south, the spirit is naturally produced chiefly from wine, and in the north, from different kinds of grain, the different materials used giving rise to the distinctive flavours characteristic of the spirits of different countries.

In Scotland the manufacture of whiskey was a subject for legislation as early as the sixteenth century, and extracts from the statutes show that 'aqua vitæ' was not the exclusive product of malted barley, but that unmalted grain was also used in the early days of spirit distillation in Scotland, and this has been the practice in Ireland up to the present day.

In 1805, during the Napoleonic wars, and owing no doubt to the possibility of a shortage in the supply of grain for food, the use of grain for the manufacture of spirits was prohibited throughout the United Kingdom.

In both Scotland and Ireland the pot-still was used prior to the invention of the patent continuous still by Aeneas Coffey in 1831, since when the patent still has been increasingly employed for the manufacture of spirit from a mixture of malt and unmalted grain, and known locally as 'whiskey.' About two-thirds of the potable spirit made in Scotland and Ireland at the present time is of this description. The spirit produced from other materials as molasses, rice, starch, potatos, dates, currants, &c., is almost invariably distilled from a 'patent still,' and is used chiefly for industrial purposes. This applies particularly to the spirit made in the English distilleries (about eight in number), where patent stills are almost exclusively employed. When *malt only* is used the whiskey is produced in Scotland chiefly, and in Ireland exclusively, from pot-stills. In Scotland there are 150 distilleries, 137 of which use pot-stills only; 10, patent-stills; and 3, both pot and patent-stills. In Ireland, out of 27 distilleries, 18 use pot-stills only; 2, patent-stills only; and 7, both pot- and patent-stills.

The different characters of the various kinds of whiskey are due to the presence of small amounts of secondary products, sometimes referred to as 'impurities' or 'by-products' (as esters, higher alcohols, &c.), rarely exceeding in the aggregate one-half p.c. of the ethylic alcohol present, but sufficient to impart a distinctive flavour and aroma to the spirit.

These differences in character depend mainly upon (*a*) the kind and relative proportions of the materials used in the wash; (*b*) the methods of mashing and fermentation employed; and (*c*) the type of still used and the manner in which it is worked.

For the processes of mashing, fermentation, and distillation employed in the manufacture of ordinary alcohol, and for a description and diagram of Coffey's patent still, *see* article ALCOHOL.

This is known as 'silent' or neutral spirit, but grain spirit, distilled from patent stills, when intended for potable purposes, is not so highly rectified as to be deprived of its 'whiskey' character.

In the manufacture of pot-still whiskey in Scotland, barley-malt is practically the only material employed in the mash, whilst in the Irish pot-still distilleries the mash consists of a mixture of barley-malt with unmalted barley or other grain. The proportions vary with a view to securing particular flavours in the whiskey, but a typical mash consists of about four-fifths barley (malted and unmalted), and one-fifth of wheat, oats, and rye, the proportions decreasing in the order of enumeration. Maize is generally excluded from the pot-still whiskies.

Besides the formation of sugar by the action of diastase during the mashing process, other substances, the exact nature of which is not thoroughly understood, are obtained in solution, from which the secondary constituents of the finished whiskey are both directly and indirectly derived. According to Bell (Select Committee of the House of Commons on British and Foreign Spirits, 1890–1) some of the essential oils naturally existing in the malt and grain, and the empyreumatic and creosotic bodies with which the malt becomes impregnated during the process of drying over peat, anthracite, or coke fires, pass through the operations in a more or less chemically unchanged condition, thus imparting distinctive characters to the whiskey, particularly when the ordinary pot-still is employed for the distillation.

Similarly during the process of fermentation, the conversion of the sugar into ethyl alcohol is accompanied by other chemical changes resulting in the formation of substances which also influence the flavour of the finished whiskey. Of these the principal are the higher alcohols, which have been shown by Ehrlich and others to be due to the splitting up of certain nitrogenous substances (amino acids) produced by the peptonising action of the malt in the mashing process. The ultimate result is affected by the special nature of the yeast, the temperature at which it works, and the time occupied in fermentation.

The simplest form of pot-stills employed in Scotland are heated by direct fire, and have no special means of rectification. The long neck of the still, however, although originally designed simply to prevent particles of the boiling mash being mechanically carried over by frothing or spraying, incidentally has the further important practical use of effecting considerable rectification.

The pot-stills sometimes have their rectifying power increased by means of perforated plates placed transversely in the neck of the still, or by the use of 'purifiers,' pipes or circular vessels cooled by water and fitted between the neck of the still and the condenser.

Some stills are heated by means of steam-jackets or coils instead of direct fire, and this difference in the method of heating is said to have an important influence on the flavour of the whiskey. Certain empyreumatic bodies are thought to be generated by the open fire method, but according to Bell, Schidrowitz, and Thorpe, these are more probably derived from the peat or coke used for heating the malt kilns.

In the manufacture of Scotch whiskey, two distillations only are usually made, first from the 'wash still' from which the whole of the volatile constituents are collected as 'low wines'; and second, from the 'low wines still,' the distillate from which is collected in three fractions, viz. (1) 'foreshots,' (2) clean spirit or 'whiskey,' and (3) 'feints.' The first and third fractions are added to the low wines of the next distilling period, and so on throughout the distilling season, the residue left in the wash still ('pot ale'), and that in the low-wines still ('spent lees') being run to waste.

The whiskey is generally run off at a strength of 11–25 overproof, but in the Lowlands, where a third distillation or 'rectification' is generally made, the strength of the whiskey distillate is from 40 to 45 overproof.

In Ireland the pot-stills are generally much larger than in Scotland, having sometimes a capacity of 20,000 gallons. The head of the still is shorter, and the still for low wines and feints is provided with a 'lyne arm,' or long pipe which passes through a tub of water, the liquid thus condensed between the head of the still and the worm being conveyed by a 'return pipe' to the body of the still. By this means a considerable degree of rectification is effected.

Three distillations are the rule for Irish pot-still whiskey, and the fractions are more numerous than in the manufacture of Scotch whiskey, consisting of strong low wines, weak low wines, strong feints, and weak feints. The middle or 'whiskey' fraction is also run off at a higher strength than in the Scotch process, viz. from 24 to 30 overproof.

The point at which the collection of foreshots is stopped and that of whiskey commenced, as well as that at which the running of whiskey ceases and the collection of feints begins, is determined by the judgment and experience of the distiller, but various simple devices are employed for testing the distillate at different stages, as glass floats or hydrometers, specific gravity beads, and samplers for testing the distillate by dilution with water and observing whether the mixture is opalescent or clear.

Scotch whiskeys may be divided into the following five principal classes: (1) Highland malts; (2) Lowland malts; (3) Campbeltowns; (4) Islays; all made from malt in pot stills; and (5) grains, a name given to patent-still whiskeys. *Irish whiskeys* have no corresponding classification, all the 'self' or non-blended whiskeys being sold under distinctive names.

The secondary products, and therefore the character of the spirit, are considerably affected by the strength at which the whiskey is run off. Some of these products (especially esters) suffer partial decomposition in both the mash and low wines stills, whilst others, of higher boiling-point, remain in the stills and are run to waste with the pot ale and spirit lees. More than two-thirds of the secondary products are lost in this manner, only from 10 to 30 p.c. passing into the finished whiskey. (For the recovery and utilisation of the esters left in still residues, *see* art. RUM.)

It has not yet been found possible to trace any definite relationship between the commercial characteristics of various pot-still whiskeys, and their composition as ascertained by analysis, for the reason that the secondary constituents are not individually identified by chemical analysis, but are assessed in groups consisting of members of the same family though in varying proportions, *e.g. acids, aldehydes, esters*, and *higher alcohols*.

There is some reason to believe, from the researches of Guareschi and Mosso (on behalf of the Italian Government), Vaughan of Michigan University, and Husz of Sweden, that other bodies may be present due to decomposition of albuminous matter in the grain and having alkaloidal properties. They are alleged to be largely accountable for the deleterious effects of spirit drinking, but, if present, they occur in such minute quantities as to elude identification hitherto.

Husz attributed the unusually deleterious character of the spirits drunk in Sweden in a certain year to the use of unsound grain, and Lombroso has shown that an alkaloid having an action like strychnine is generated in decaying maize. Lauder Brunton, whilst attributing much of the harmful effects of new spirit to furfural, also supports the theory that these effects may be partly due to the presence in minute quantities of alkaloidal bodies, especially in potato spirit.

Schidrowitz has determined the percentage of nitrogen in new pot-still whiskies with the results shown below, but failed to detect the least trace of substances giving alkaloidal reactions. The nitrogen is calculated as NH_3, and expressed as grams per 100 litres of absolute alcohol—

Highland malts	0·09–0·19
Lowland malts	0·11–0·30
Campbeltowns (malt) . .	0·08–0·14
Grains	0·03–0·14
American rye whiskies (matured)	0·26–0·39

No definite evidence was, however, obtained by the Royal Commission on Whiskey, &c., that the deleterious effects attributed to the consumption of spirits are directly due to the presence of poisonous secondary products, and the bulk of the medical evidence was to the effect that the actual amount of the secondary products is so small compared with that of the ethyl alcohol, that the physiological effects produced by them must also be extremely small in comparison with those due to the ethyl alcohol itself. It would appear to follow, therefore, that whiskey derived either from pot or patent still has much the same toxic effect if taken in the same quantity and at the same alcoholic strength.

At the same time, since many substances are known to produce marked effects on the digestive system merely as a result of the sensation produced by their *flavour*, this plays an important part from a dietetic point of view, and the more agreeable flavour of a mature whiskey may exert a favourable mental effect which promotes the activity of the digestive processes, whilst the unpalatable flavour of new 'silent' or neutral spirits may tend to interfere with digestion apart from the direct effect due to the alcohol itself.

The methods usually employed for the estimation of the different groups of secondary constituents are given in detail in the Minutes of Evidence taken by the Royal Commission on Whiskey and other Potable Spirits, 1908–9, vol. ii. App. Q, xii. Thorpe; *see* also vol. i. App. F. Schidrowitz.

The following tables give the results of analyses of various kinds of whiskey by Schidrowitz, Tatlock, and Thorpe, expressed in all cases as parts by weight in 100,000 parts by volume of absolute alcohol (*e.g.* grams per 100 litres).

Schidrowitz and Kaye's results of analyses of 100 samples of the principal classes of *Scotch pot-still whiskey* are summarised in the following table, showing the minima, maxima, and averages—

No. of samples	Description	Total acid	Esters	Higher alcohols (A–M)	Aldehydes	Furfural	Average total 'impurities'
39	Highland malts .	10–83	33–185	112–235	4–66	1·6–6·3	292
16	Lowland malts .	6–60	27–87	82–228	8–54	0–5·2	255
16	Campbeltowns .	12–100	53–140	160–259	11–85	2·4–8·0	335
5	Islays . . .	15–36	40–86	155–200	17–40	3·8–5·2	294
24	Grains . .	3–69	20–55	33–80	trace–17	0–0·9	120
100	Average . .	30·9	60·6	143	18·6	3·2	252

ANALYSES OF IRISH POT-STILL WHISKEY (Schidrowitz).

Description	Total acid	Esters	Higher alcohols (A–M)	Aldehydes	Furfural	Total
A. New	7	34	145	12	5·5	203
„ 13 years' plain wood	29	38	185	68	3·3	323
B. New	6	28	233	8	4·1	279
„ 13 years' plain wood	32	47	264	21	4·4	368
C. 14 years sherry	87	87	226	32	4·5	436
D. Mature	67	59	147	16	2·6	291
Average	38	49	200	26	4·1	317

SCOTCH PATENT STILL WHISKEYS (Schidrowitz).

Description	Total acid	Esters	Higher alcohols (A–M)	Aldehydes	Furfural	Total
New whiskey	4	25	65	2	—	96
4 months' sherry wood	24	26	31	4	0·07	85
2 years' plain wood	14	25	100	5	trace	144
2 years' sherry wood	58	40	44	7	0·15	149
Average	25	29	60	4·5	0·05	118·5

Irish Patent Still Whiskeys (Schidrowitz).

Description	Total acid	Esters	Higher alcohols (A–M)	Aldehydes	Furfural	Total
Distillery A—new	17	25	38	—	—	80
,, ,, ...	21	41	50	—	trace	112
,, 2 years	10	24	48	3	trace	85
Distillery B—new	3	19	52	—	—	74
,, 1¼ years	9	25	46	1	trace	81
Distillery C—new	—	33	50	11	—	94
Average	10	28	47	2·6	trace	87·6

The following analyses by Tatlock show the maxima, minima, and averages obtained from 75 samples of Scotch and Irish malt-pot-still whiskeys, grain patent still, American, and blended whiskeys—

	Highlands, 31 samples	Lowlands, 9 samples	Islays, 4 samples	Campbeltowns, 2 samples	Irish, 2 samples	American, 4 samples	Grains, 7 samples	Blends, 16 samples
Esters—								
Maximum . .	154·16	85·80	78·05	85·62	44·22	119·52	50·90	92·05
Minimum . .	45·01	34·52	48·31	61·42	38·42	111·06	22·04	33·56
True average .	83·06	66·19	61·51	73·52	41·32	115·99	33·26	58·96
Higher alcohols—								
Maximum . .	190·40	240·66	161·70	206·70	169·10	177·34	68·47	111·25
Minimum . .	73·51	103·49	130·20	139·58	154·93	102·55	32·47	48·71
True average .	144·61	140·40	144·55	173·14	162·01	156·99	45·32	80·76
Volatile acids—								
Maximum . .	89·06	39·86	32·41	56·35	49·23	132·11	32·93	100·13
Minimum . .	21·76	4·70	17·11	31·16	4·55	65·24	2·86	13·12
True average .	41·78	17·35	25·86	43·75	26·89	99·43	16·67	40·61
Aldehydes—								
Maximum . .	35·06	33·59	31·74	33·54	21·12	32·85	12·95	26·60
Minimum . .	3·21	4·70	19·82	32·45	4·34	17·01	1·59	1·26
True average .	19·48	20·42	28·40	32·99	12·73	26·53	7·66	9·29
Furfural—								
Maximum . .	7·34	5·85	6·29	3·77	3·02	3·86	0·50	3·17
Minimum . .	1·58	2·65	3·25	3·23	2·73	1·95	0·10	0·43
True average .	4·19	4·39	5·02	3·50	2·87	3·00	0·25	1·63
Total secondary products—								
Maximum . .	382·35	314·81	294·99	385·98	269·62	452·92	130·38	267·64
Minimum . .	218·94	218·52	225·94	267·84	222·04	328·76	68·04	106·22
True average .	294·41	282·03	265·37	326·91	245·83	396·89	102·08	191·25

The results of analysis of 7 samples of high-class whiskeys as supplied by Government contractors for hospital use are given in the following table (Thorpe):—

Age	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total
7 years .	28·2	9·6	90·0	175·5	2·7	306·0
,, .	28·2	9·6	87·9	175·5	2·7	303·9
,, .	28·2	9·6	90·0	175·5	2·7	306·0
10 years .	24·3	12·1	92·1	877·1	3·5	1009·1
,, .	31·5	9·8	93·0	300·0	3·3	437·6
,, .	32·9	9·8	114·0	456·1	3·3	616·1
,, .	41·0	12·1	124·5	578·9	3·1	759·6
Average	30·6	10·4	98·8	391·2	3·0	534·0

Results of analyses of 5 samples of spirits made in Germany and sold as cheap whiskey in Hong Kong are given on p. 754.

Samples A and B consisted of 'silent' spirit, with an admixture of pot-still whiskey for the purpose of imparting the genuine flavour of whiskey. They are very similar to what is usually sold as 'whiskey' in public houses in England. Samples C, D, and E consisted of highly rectified 'silent' spirit coloured and flavoured to imitate whiskey. The fusel-oil impurities were much less than is usually found in genuine Scotch and Irish pot-still whiskeys of high commercial quality, whilst furfural and other aldehydes were practically absent, and there was no evidence that these spirits contained anything of a deleterious nature apart from the alcohol itself.

'Pot-still' and 'patent-still' spirits (Thorpe, Royal Comm. on Whiskey and other Potable Spirits, App. Q, vi., vii., viii.). An examination

Secondary products	A	B	C	D	E	Average
Volatile acidity (as acetic acid) .	50·7	63·7	10·5	14·0	7·0	29·2
Furfural	1·5	1·2	Nil	Nil	Trace	0·5
Aldehydes (as acetic aldehyde) .	1·8	2·1	Trace	Trace	Trace	0·8
Esters (as acetic ester) . .	87·5	109·5	15·0	7·8	3·6	44·7
Higher alcohols	225·7	205·4	20·4	22·6	33·2	101·4
Total secondary constituents .	367·2	381·9	45·9	44·4	43·8	176·1

of the tables, pp. 755, 756, giving the results of the analyses of a number of representative samples of both kinds of spirits shows very clearly the broad distinction between the 'pot-still' and 'patent-still' spirit.

There is always a much larger amount of the secondary constituents in the 'pot-still' spirit. Speaking generally, the percentage of every one of the secondary constituents usually determined is greater in the 'pot' than in the 'patent' spirit, but the most marked differences are in the 'higher alcohols' and 'furfural.' 'Patent' spirit contains no furfural when new, although after storage in wooden casks it is sometimes found to contain traces of this substance, but always in much smaller amount than in 'pot-still' spirit, in which it is never absent. The low percentage of the 'higher alcohols,' and the absence of all but mere traces of furfural render it a comparatively easy matter to distinguish 'patent' from 'pot-still' spirit. But the variations in the amounts of the secondary constituents in both classes of spirits renders it less easy to estimate the exact proportion of each kind of spirit present in mixtures. Comparing the 'pot-still' spirits among themselves, it will be observed that there are considerable variations in both the total amount and in each constituent of the secondary bodies. The Scotch whiskeys generally show a somewhat less total amount than the Irish, and the Speyside, Banffshire, and Highland samples have a rather smaller amount than the Islay and Campbeltown samples. The latter, as well as most of the Irish samples, are mainly 'blending' as distinguished from 'self' whiskeys.

The differences between new and old 'pot-still' whiskeys, so far as shown by analysis, are mainly in the increased amounts of the volatile acids and aldehydes, and to a less extent of the esters found in the old spirit when stored in wooden casks. The higher alcohols and furfural appear to remain very much the same. Any changes that occur in 'patent' spirit are of a similar kind.

'Pot-still' whiskey is almost always stored in sherry casks, or in other well-seasoned wooden casks that have formerly contained similar spirit. A large proportion of the increases in the secondary constituents which occur in spirit stored in such casks takes place in the first few months, and is due to a process of extraction of these products absorbed in the wood of the casks from former spirits. This absorption is to some extent selective. The ethyl alcohol slowly diffuses through the wood of the cask and passes into the air, leaving some of the esters and higher alcohols behind in the wood, which thus becomes more or less charged with the secondary constituents, according to the length of time and other circumstances attending the storage of spirit in the warehouse.

Probably also, especially when the casks are empty, there is some production of acids, aldehydes, and esters by the slow oxidation of alcohols in the wood of the casks.

A comparison of the ordinary 'patent' spirits with British and foreign spirits of high strength which are not usually stored in wooden casks, but in metal drums or vats, shows that the latter spirits contain still less of the secondary constituents, and that the slight changes which occur in ordinary patent spirits do not take place in these high strength spirits. These spirits are used mainly for technical and industrial purposes, and are often of very great purity, although made from molasses, potatos, and beetroot sugar residues, or other materials not employed for making spirits intended for consumption in this country.

Maturation or *ageing*. In addition to the changes above referred to in the secondary constituents due to storing in casks, there are other changes due to the presence of substances not included in the ordinary analysis of spirits, but which have much to do with the difference in flavour of new and old whiskeys. Thorpe, for example, found indications of pyridine bases, allyl alcohol, and allyl aldehyde derived from the peat used as fuel in malting, and acrolein, due either to the fat in the wash extracted from the grain or possibly from the soap which is occasionally added to the contents of the still to prevent frothing. Schidrowitz found in new pot-still whiskey distinct evidence of the presence of pyrrole, phenolic bodies, an alkaline substance (probably an ammonium salt), sulphuretted hydrogen, sulphurous acid, and a trace of nitriles. All of these are readily changed on exposure to air and moisture, as in storage in casks. The pyrrole probably resinifies, the phenols interact with aldehydes, acids, and alcohols, forming condensation products; the sulphuretted hydrogen and sulphurous acid would readily oxidise, and the nitriles (if present) rapidly condense or be transformed into acids. None of these substances was found in mature spirit.

Numerous processes have been suggested for the artificial ageing or maturing of whiskey. These are, for the most part, oxidation processes, as by treatment with charcoal, or (as in Carroll's process) by passing the spirit vapour mixed with air, and superheated to 300°F. through a pipe enclosed in a steam jacket also heated to 300°F. Hewitt's method, which is a de-aldehyding process, consists of the addition of phenylhydrazine-sulphonate of sodium or calcium to the low wines still, by which means the aldehydes, including furfural, are held back, and the amount of these passing into the distillate considerably reduced. The effect of all these processes is to remove the harsh flavour of new spirits and impart the softer character of mature whiskey, thus accelerating the time when the spirit becomes ready for consumption as a beverage, but without necessarily imparting to it the true characteristic flavour of whiskey which has been matured by long storage.

The changes in the secondary products due to storage of whiskey in wooden casks and bottles are shown by Thorpe in Appendix Q, ix., x., xi. The results show that there is a well-marked increase in each of the secondary constituents during the first six months' storage. After 9–12 months the higher alcohols and furfural remain practically constant, and the increases in the other constituents were very slow. After about 18 months the differences were within the limits of experimental error. Practically no change occurs in spirits stored in glass bottles.

Crampton and Tolman (J. Amer. Chem. Soc. 1908, 30, 98) examined the spirit stored in casks by sampling annually for a period of 8 years, and found an increase in the higher alcohols due to the fact that the wood was less pervious to these than to ethyl alcohol and water. The other secondary constituents increased rapidly for 3 or 4 years, and then only very slowly. An increase of furfural was probably due to the charred wood of the interior of the casks. It

Spirits from Pot Still Distilleries (Thorpe).

No.	Age	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total	District
1	New . .	16·9	9·2	77·4	407·2	2·9	513·6	Speyside.
2	6 years .	52·2	19·6	93·9	472·1	1·9	639·7	,,
3	New . .	13·2	5·4	63·2	471·4	2·9	555·1	Banffshire.
4	7 years .	53·6	32·2	91·0	371·4	1·9	550·1	,,
5	New . .	9·8	9·8	63·1	490·0	2·8	575·5	,,
6	,, . .	15·0	21·8	63·8	451·6	4·2	556·4	—
7	7 years .	30·1	41·6	92·0	460·5	3·6	627·8	Islay.
8	,, . .	46·0	43·2	99·0	563·2	3·6	755·0	—
9	New . .	17·0	33·6	72·9	410·9	3·5	537·9	—
10	4 years .	37·5	34·8	81·4	453·0	3·3	610·0	Campbeltown.
11	10 years .	47·3	10·0	98·8	322·8	5·7	484·6	Highland.
12	New . .	3·3	50·2	102·8	522·6	3·1	682·0	Irish.
13	6 years .	32·6	55·9	86·4	771·2	2·9	949·0	,,
14	New . .	1·7	26·3	73·7	861·4	2·2	965·3	,,
15	,, . .	1·7	8·7	73·0	729·8	0·1	813·3	,,
16	8 years .	17·5	10·5	30·0	894·7	3·1	955·8	,,
17	New . .	4·2	7·0	13·6	701·7	1·1	727·6	—
18	6 years .	21·0	12·2	35·0	789·0	1·4	858·6	Irish.
19	New . .	1·4	4·6	75·9	336·9	Nil	418·8	,,
20	1 year . .	5·2	7·0	106·6	571·9	,,	690·7	,,
21	New . .	1·4	11·5	46·1	857·9	8·5	925·4	,,
Average . .		20·4	21·7	73·3	567·3	2·8	685·3	

Patent Still Grain Spirits (Thorpe).

No.	Age	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total	District
1	New . .	1·9	9·6	30·8	39·0	Nil	81.3	Scotch Distillery
2	7 years .	19·0	10·8	35·0	21·8	0·1	86·7	,,
3	,, . .	36·9	12·0	47·9	21·1	0·3	117·2	,,
4	New . .	1·9	4·7	41·1	97·8	Nil	145·5	,,
5	4½ years .	15·6	14·1	46·4	81·3	,,	157·4	,,
6	New . .	3·8	trace	22·8	14·0	,,	40·6	,,
7	3 months .	5·2	,,	45·6	42·0	,,	92·8	,,
8	New . .	3·5	,,	12·2	28·0	,,	43·7	,,
9	7 years .	40·0	3·3	22·8	57·8	0·3	124·2	Irish Distillery.
Average . .		14·2	6·1	33·8	44·6	0·1	98·8	

Patent Still Spirits of High Strength (Thorpe).

No.	Description	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total
1	British spirit from molasses . .	1·2	35·1	62·5	84·0	Nil	182·8
2	British spirit from grain, highly rectified	1·2	trace	11·1	21·2	,,	33·5
3	British spirit from molasses, highly rectified	1·2	3·5	7·3	63·0	,,	75·0
4	British spirit crude, from molasses .	2·5	97·3	187·7	20·9	,,	308·4
5	Foreign spirit imported from Hamburg.	1·2	Nil	5·5	10·4	,,	17·1
6	Foreign spirit imported from Hamburg.	1·2	Nil	9·1	20·9	,,	31·2
7	Foreign spirit imported from Stettin	1·2	2·2	7·2	83·7	,,	94·3
	Average	1·4	19·7	41·5	43·4	,,	106·0

was found also that water passed through the wood of the cask more rapidly than the ethyl alcohol, thus giving rise to an *increase in strength*. This is unusual and was no doubt due to the exceptionally warm and strongly ventilated place of storage.

American whiskey. The United States Pharmacopœia prescribes the following requirements for whiskey. It should be at least 2 years old; its sp.gr. should lie between 0·930 and 0·970; its alcoholic content should be not less than 44 p.c., nor more than 55 p.c. by weight; its residue not more than 0·25 p.c.; the residue from 100 c.c., which should be neither sweet nor spicy, should dissolve in 10 c.c. of cold water, and this solution should be coloured only a pale green when treated with a drop of very dilute ferric chloride solution (a deeper colour would indicate more than traces of tannin). In evaporating the liquor on the water-bath for the residue, the last traces volatilised should have an agreeable odour free from harshness, indicative of the absence of fusel oil. Its reaction should be slightly acid, but not more than 1·2 c.c. of deci-normal alkali should be required to neutralise 100 c.c. of the liquor using phenolphthalein as indicator.

Rye whiskey is made in the United States and Canada from rye and malt only. *Bourbon whiskey* (so-called from Bourbon County, Kentucky, where it was originally made) is prepared from a mixture consisting of 50–60 p.c. maize, 10 p.c. malt, and the remainder rye.

The following table gives the results of analysis of Bourbon and rye whiskeys by Schidrowitz:—

Description	Total acid	Esters	Higher alcohols (A–M)	Aldehydes	Furfural	Total
Bourbon whiskey—5 years . .	126	99	197	11	2·2	435
,, ,, mature . .	122	78	129	14	3·0	346
Rye whiskey—7 years . . .	140	134	277	20	3·9	575
,, ,, mature . . .	160	141	268	18	3·4	590
,, ,, ,, ...	135	125	187	21	3·9	472
,, ,, ,, ...	82	71	150	13	3·6	320
,, ,, 10 years . . .	70	79	98	11	2·7	261
Average . . .	119	104	172	15	3·2	428

Results of analyses of 188 samples of new and old Bourbon and rye whiskey examined in the laboratory of the United States Department of Agriculture (Wiley) are shown on next page.

Imitation whiskey is sometimes prepared from strong neutral or 'silent' spirit diluted to the proper strength and flavoured with certain essential oils or artificial fruit essences, as oil of wintergreen, œnanthic and pelargonic esters, and coloured with caramel. Prune juice is sometimes added to give 'body' to this mixture.

Fleischman quotes the following as a recipe for a low grade 'blended whiskey': spirits, 32 gallons; water, 16 gallons; caramel, 4 oz.; beading oil, 1 oz. 'Beading oil' (so-called from its use in producing an artificial bead on cheap liquors) is prepared by mixing 48 oz. of sweet oil of almonds with 8 oz. of commercial sulphuric acid, neutralising with ammonia, adding double the volume of proof spirit, and distilling the mixture (The Art of Blending and Compounding Liquors and Wines, New York, 1885).

Adulteration of whiskey. Under the Sale of Food and Drugs Act, whiskey (like brandy and rum) may not be sold below a strength of 25 p.c. under proof unless the fact of dilution is notified,

Description	Total acid	Esters	Aldehydes	Furfural	Higher alcohols (A. M.)	Total
New rye whiskeys (19 samples)—						
Average	11·4	50·6	17·8	2·4	266·4	348·6
Maximum	28·2	132·8	86·0	5·2	378·4	
Minimum	2·6	8·8	0·0	0·0	187·0	
Old rye whiskeys (76 samples)—						
Average	147·6	137·0	27·6	4·6	352·0	661·8
Maximum	312·4	287·4	47·2	14·0	585·8	
Minimum	72·8	60·0	4·4	0·8	146·6	
New Bourbon whiskeys (18 samples)—						
Average	16·4	45·0	7·8	1·7	229·4	300·3
Maximum	39·2	112·8	36·2	12·8	343·4	
Minimum	3·6	1·8	0·0	trace	70·6	
Old Bourbon whiskeys (75 samples)—						
Average	137·6	103·6	19·4	3·8	287·2	551·6
Maximum	203·8	209·0	46·4	16·2	517·0	
Minimum	69·4	39·0	7·2	1·4	50·4	

and the great majority of prosecutions under the Act for the adulteration of whiskey are on account of dilution with water below the legal limit of strength. For the method of calculating the degree of dilution, *see* art. Brandy.

Sometimes a neutral or 'silent' spirit made from substances other than grain (as potatos, beet-sugar residues, &c.) is mixed with sufficient genuine whiskey to give it a more or less whiskey character, and such adulteration is best detected by expert tasting ('degustation') combined with a determination of the secondary constituents and a comparison of the relations which they bear to each other.

Amongst the various substances alleged to have been used for the grosser forms of adulteration may be mentioned creosote, fusel oil, methylated spirit, sulphuric acid, and salt. Traces of copper, tin, and lead have been found as accidental impurities derived from the stills and other apparatus employed.

In consequence of representations made as to the deleterious character of the whiskey sold in public-houses in the poorer class districts of the larger towns in England, Scotland, and Ireland, and at fairs and markets, particularly in the west of Ireland, an investigation into the matter was made a few years ago by the Excise Authorities. Nearly 100 samples were taken from all parts of the United Kingdom and analysed in the Government Laboratory, but, apart from the fact that most of these consisted mainly of plain patent-still spirit, no evidence of the presence of the deleterious adulterants above referred to could be found.

The results of analyses (showing the maxima, minima, and averages) are summarised in the following table (Thorpe):—

	Volatile acid	Aldehydes	Esters	Higher alcohols	Furfural	Total
England (38 samples)—						
Maximum	25·1	22·5	127·9	310·5	1·9	370·7
Minimum	1·4	2·2	30·1	11·2	Nil	67·0
Average	7·3	9·0	52·2	95·8	0·7	165·0
Scotland (23 samples)—						
Maximum	18·0	23·8	85·7	179·6	1·6	260·6
Minimum	1·2	1·7	30·8	43·7	Nil	77·8
Average	6·1	10·5	47·2	88·2	0·5	152·5
Ireland (30 samples)—						
Maximum	54·6	37·2	71·5	649·2	4·2	767·3
Minimum	1·4	2·4	29·5	32·2	Nil	73·3
Average	8·2	11·1	47·8	232·0	1·2	300·3

There is no legal definition of 'whiskey' in the United Kingdom, but numerous suggestions were made by witnesses before the Select Committee on British and Foreign Spirits in 1890–1, and the Royal Commission on Whiskey and other Potable Spirits in 1908–9, differing essentially in principle and depending chiefly upon the point of view of the witness.

The strictest definition suggested was that 'whiskey' should be manufactured in a pot still exclusively and from certain prescribed materials grown in the country, as malted barley alone in the case of 'Scotch' whiskey, and malted barley with unmalted grain (barley, wheat, oats, or rye) in the case of 'Irish' whiskey.

Others would admit patent-still spirit,

restricting, however, the materials to cereal grains (including maize), and the saccharifying agent to the diastase of malt, whilst in a few cases the extreme view was held that no restriction should be imposed either on the materials used or the process of distillation.

Since much of the barley used in both Scotland and Ireland is of *foreign* growth, the definition of Scotch and Irish whiskey cannot well exclude the use of foreign grain, and therefore maize (which came into use in 1846 immediately after the repeal of the Corn Laws) is not excluded in the manufacture of 'whiskey.'

With respect to the blending of patent-still spirit made from grain with pot-still spirit, it was held that since whiskey (consisting as it does of alcohol and water, with certain by-products derived from malt and grain) does not cease to be whiskey when diluted with water, so the addition of patent-still spirit, also made from grain, does not remove the mixture out of the category of 'whiskey.'

After full consideration of all the evidence the Royal Commission of 1908–9 arrived at the following conclusions and definitions:—

(1) That the term 'whiskey' having been recognised in the past as applicable to a potable spirit manufactured from (*a*) malt, or (*b*) malted and unmalted barley or other cereals, the application of the term 'whiskey' should not be denied to the product manufactured from such materials.

(2) That no restrictions should be placed upon the processes of, or apparatus used in, the distillation of any spirit to which the term 'whiskey' may be applied as a trade description.

(3) *Definition.* 'Whiskey' is a spirit obtained by distillation from a mash of cereal grains saccharified by the diastase of malt; that 'Scotch whiskey' is whiskey, as above defined, distilled in Scotland; and that 'Irish whiskey' is whiskey, as above defined, distilled in Ireland.

J. C.

WHITE ANTIMONY. *Valentinite v.* ANTIMONY.

WHITE ARSENIC. *Arsenious oxide v.* ARSENIC.

WHITE COPPERAS. Native *ferric sulphate* or *coquimbite* $Fe_2(SO_4)_3,9H_2O$.

WHITE IRON PYRITES. *Ferric sulphide* or *marcasite* FeS_2 *v.* IRON.

WHITE LEAD *v.* LEAD; also PAINTS and PIGMENTS.

WHITE LEAD-ORE *v.* CERUSSITE.

WHITE METAL *v.* TIN.

WHITE MUNDIC. *Mispickel v.* ARSENIC.

WHITE PRECIPITATE. *Mercuric ammonium chloride v.* MERCURY.

WHITE VITRIOL. *Zinc sulphate* $ZnSO_4,7H_2O$ *v.* ZINC.

WHITING *v.* CHALK.

WIIKITE. A rare mineral consisting of tantalic and titanic acids, zirconia, silica, cerium, and yttrium earths, thoria, uranic oxide, ferrous oxide, &c., and of interest in containing scandium (Sc_2O_3, 1·17 p.c.) in relatively large amount. It is a black, brown, or yellow, amorphous mineral resembling euxenite or yttrotantalite in appearance, and has been found, together with monazite, in a felspar quarry at Impilaks, Lake Lagoda, Finland. It supplied the material for Crookes's work on scandium (Proc. Roy. Soc. 1908, A, 80, 516; Phil. Trans. 1908, A, 209, 15). Orthite from the same locality has also been found to contain 0·8–1·0 p.c. of scandia (R. J. Heyen, Sitz-Ber. Akad. Berlin, 1911, 379). More recently (Dec. 1911) a mineral containing scandium as an essential constituent has been described (*v.* THORTVEITITE).

L. J. S.

WILLEMITE. A mineral consisting of zinc orthosilicate Zn_2SiO_4, crystallising in the rhombohedral system (with parallel-faced hemihedrism). It is abundant at Franklin Furnace, and Sterling Hill in New Jersey, where it is mined, together with zincite and franklinite, as an ore of zinc (ZnO, 73 p.c.). At a few other localities it is of sparing occurrence. It varies considerably in colour, being yellowish, apple-green, flesh-red, &c.; the lustre is vitreous to resinous; sp.gr. 4·0–4·1. *Troostite* is a variety containing up to 10 p.c. of MnO replacing the zinc oxide. When struck with a hammer or when exposed to the emanations of a radium salt, the mineral displays a brilliant green phosphorescence.

L. J. S.

WILLESDEN FABRICS AND PAPER *v.* CELLULOSE.

WILLOW BARKS *v.* TANNINS.

WINE. Wine, strictly speaking, is the fermented juice of the fruit of *Vitis vinifera.* The term *British wines* is applied to beverages made after the manner of wine from substances other than the juice of fresh grapes.

The vine is cultivated for the manufacture of wine in the middle and south of Europe, the northern and southern extremities of Africa, some of the western parts of Asia, the islands of the Atlantic, portions of America—from the Potomac in the north to the centre of Mexico in the south—in California, and in Australia. The number of varieties is very large; but experience shows that the vines employed in particular districts should either be indigenous to those districts or be improved varieties of the indigenous strain. Thus, European vines when tried in America were but partially successful; whilst, on the other hand, American vines transplanted to the Gironde degenerated and yielded no potable wine. The vine grows on chalky, silicious, aluminous, and magnesian soil, best along the borders of rivers, and on ground which, though not itself soaked with water, can constantly attract it from the subsoil.

Vintage and vinification. The methods of procedure vary with the character of the wine —*i.e.* whether white or red wine is to be produced. The practice as regards the period of ripeness at which the grape is gathered varies considerably; thus, in the case of champagne, where the greatest attainable paleness is desired, the grapes are gathered before the point of fullest maturity, whereas the wines of Burgundy are vintaged when the grapes produce the deepest colour. Wines from imperfectly-ripened grapes require longer time to mature after manufacture, and, theoretically speaking, the grapes should hang until excessive dryness or danger of frost threatens; but other and conventional considerations, such as colour, have to be taken into account. In exceptional instances, as in the Sauterne district, those berries only are cut out of the bunch which have attained the desired point of ripeness; but the common practice is to gather all the grapes carried by the vines, the vintagers either separating immature and spoiled berries as they proceed, or carrying the whole bulk to a kind of specialist, who performs this part of the labour. Whichever course may be taken, the selected fruit is carried to the press house, and the question then arises whether the stalks are to be removed or pressed with the grapes. In the case of white wines the almost universal practice is to leave the grapes upon the stalks, for the reason that the resulting liquor is almost at once separated from the marc, and before the astringent principle of the stalks can be communicated to it, whereas red wines must be allowed to remain upon the marc for some time, and the stalks are removed. The commonest mode of separation is to cause the grapes to pass through a series of sieves, by which the stalks are retained. The grapes are now crushed, either by being trodden underfoot in vats or by being passed through machines furnished with grooved rollers, the one thing to be avoided in either case being the bruising of the seeds and stalks if these have not been removed. The next process is pressing. The machines employed for this purpose were formerly boxes, so made that the must was expelled through apertures by superincumbent pressure exerted by a screw; but latterly centrifugal machines have been employed, with a saving of labour and time. In white wines the must is separated as much as possible from the marc before pressing; whilst in the preparation of champagne the grapes are not crushed at all previous to being placed in the press. In the case of red wines the colour is obtained by allowing the juice from the crushing to ferment, after which it is stirred with the grape husks, whereby the requisite amount of colouring matter ('*œnolin*' or '*œnocyanin*') is dissolved. So much of the must as can be drawn off by taps is run off by that means, and the marc is pressed; the two portions of the must are then added together. The proportion of must depends upon whether the stalks are removed or not; in the former case it is about 95–97 p.c. of the whole, in the latter it may only be 70 p.c.

The following is a summary of analyses by König of a large number of musts of different origin :—

	Specific gravity	Water p.c.	Nitrogenous matter	Sugar	Acid	Other non-nitrogenous matter	Ash
Minimum .	1·0690	51·53	0·11	12·89	0·20	1·68	0·20
Maximum	1·2075	82·10	0·57	35·45	1·18	11·62	0·63
Average .	1·1024	74·49	0·28	19·71	0·64	4·48	0·40

Fermentation.—The natural fermentation of grape juice is due to the action of a yeast (*Saccharomyces Ellipsoideus*) existing on the skin of the grape. White wines are generally fermented at a temperature of 10° or 12° in barrels with only the bunghole open for the escape of carbon dioxide. Red wines are ordinarily fermented in vats open at the top, on account of the bulk caused by the retention of the husks and the necessity of stirring, an operation variously performed during or at the completed period of fermentation, according to the district. The higher the temperature the sooner the fermentation is finished; at low temperatures a moderate fermentation takes place, which becomes more violent as the liquid becomes warmer, and reaches a maximum at 27°. By the employment of high temperatures a must rich in sugar can be converted into a wine feebly alcoholic, sweet, and yet having tasting properties. Medium musts are best fermented at from 20° to 24°, and this temperature is reached when the fermentation begins at 15°. When fermentation is completed—*i.e.* after 10 to 14 days—the liquor has become clear, the yeast cells and other suspended matters are deposited at the bottom of the vessel, and the 'young' wine is racked off and allowed to rest for some weeks.

The young wine slowly loses its sugar by after-fermentation, and albuminous substances, colouring matters, together with the acid potassium tartrate, and calcium tartrate, separate out, forming a crust known as *argol* or *argal* (*q.v.*; also TARTARIC ACID). It is then racked again into clean casks (which are often 'sulphured' before use), fined, if necessary, with isinglass or white of egg, and occasionally with dried blood or with potassium ferrocyanide. When clear it is racked again and sometimes pasteurised before being bottled or stored in casks to mature.

Influence of the 'marc' on wine. By allowing the skins and stones of ripe grapes to remain in contact with the must, the resulting wine is said to improve in bouquet, &c., and is less liable to become stale and ropy. In order to redden wine with the skins of black grapes the temperature of the wine should be between 15° and 17°. Bad grapes impart to white and red wines a brown colour. Such wines soon become turbid. Bad grapes and mildewed skins, as well as bad casks and puncheons, precipitate the red colouring matter, so that the wine becomes pale. The following are some of the cases in which the treatment of wine with 'marc' has been successful:—Wine which is muddy and cannot be clarified by the ordinary fining agents; wine in which a fining agent has been used which failed to sink to the bottom; wine which has become weak and flat; wine which is assuming or has assumed a black colour; wine having a barrel taste or a by-taste; wine which is 'corked'; wine remaining after casking off; and wine which is obtained by pressing the lees. In cases where the fermentation of new wine has been checked suddenly, the addition of marc prevents the separation of yeast (J. Nessler, Chem. Zentr. 1882, 265; Chem. Soc. Abstr. 1882, 1014).

Composition. Wine contains alcohols, glycerol, acids, salts, extractive matter, and those principles which give to it its particular colour, special flavour, smell, or bloom (*bouquet, Blume*). Whilst some of the constituents can be accurately isolated and described, others can only be detected by the smell.

The principal alcohol is ethyl alcohol. In rare instances some butyl alcohol, and in others amyl alcohol, together with ethylene glycol and *iso*butyl glycol (Henniger) are present. The quantity of alcohol in natural wines from grapes varies from 6 to 12 p.c. by weight, or from 13 to 26 p.c. proof spirit, but these limits are extended in exceptional cases. The quantity of glycerol is usually from 7 to 14 p.c., of the alcohol present.

The principal acids present are tartaric, malic, and tannic acids, due to the original grape juice, and carbonic, formic, acetic, and succinic acids, as products of fermentation.

These greatly aid in the preservation of the wine by preventing the formation of fungi. Traces of propionic, butyric, and œnanthic acids also occur in wine, together with acetaldehyde and possibly some of its homologues. Salicylic and boric acids have also been found as natural constituents of wine. As regards the origin of the fixed vegetable acids of wine, H. Brunner points out (Chem. Zentr. 1877, 4) that malic, succinic, glycollic, and oxalic acids—which are found in unripe grapes, together with tartaric acid—may either be formed by direct building up of the molecules in the plant, or their formation may be partly direct and partly indirect.

It can be demonstrated in the laboratory that the first reduction products of carbonic acid are formic and oxalic acids, and that, from the latter, we can (by the action of hydrogen) pass successively through glyoxylic, tartaric, and malic, to succinic acid, and all these acids have been found in the grape in its various stages of growth. The principal reactions may be represented as follows :—

$$2CH_2O_3+H_2=C_2H_2O_4+2H_2O;$$

Carbonic acid. Oxalic acid.

$$C_2H_2O_4+H_2=C_2H_2O_3+H_2O;$$

Glyoxylic acid.

$$2C_2H_2O_3+H_2=C_4H_6O_6;$$

Tartaric acid.

$$C_4H_6O_6+H_2=C_4H_6O_5+H_2O;$$

Malic acid.

$$C_4H_6O_5+H_2=C_4H_6O_4+H_2O.$$

Succinic acid.

Tartaric acid occurs mainly as the dextro-variety; lævo-tartaric acid is only of comparatively infrequent occurrence. If tartaric acid is not found—as, for example, in certain samples of sherry—its absence is probably due to its removal by 'plastering,' to which reference is made later on. The amount of free acid in sound wine, reckoned as tartaric acid, varies between 0·3 and 0·7 p.c. (inclusive of volatile acid, which should not exceed 0·15 p.c.); a greater amount than this imparts sourness to the wine.

The characteristic smell of wine is said to be due to œnanthic and other esters. These esters probably confer the bouquets which distinguish one vintage from another. Among them are acetopropyl, butyl, amyl, capryl, butyro-ethyl, caprylo-ethyl, capro-ethyl and pelargo-ethyl, and the tartaric esters.

According to Jacquemin (Compt. rend. 110, 1140), the characteristic bouquets of wines are due to the special characters of the yeast used in each district. One and the same must fermented with the yeast obtained from several different districts gave wines having the bouquet characteristic of the district from which the particular yeast had come.

Babo states that the bouquet of the wine from Riesling grapes is produced by the action of frost; wines from other grapes also possess a like bouquet if the grapes are frozen. Rommer (Bull. Soc. chim. [iii.] 2, 297) fermented the juice of an inferior grape and of hot-house grapes respectively with yeast cultures obtained from the Champagne, Côte d'Or, and Baxy districts, and found that in each case the wines had the bouquet of those from which the yeast has been derived. Certain of the odoriferous principles are no doubt in the nature of essential oils, which have not hitherto been isolated owing to their small amount and extremely unstable character under the influence of heat and air. In order to retain the bouquet, wines should be bottled as soon as they have attained their maximum bouquet.

According to Berthelot, the amount of the esters in wine is, after a certain time, a constant quantity independent of the nature of the alcohols and acids, but a function only of their relative amount: If A be the percentage weight of alcohol in the mixture, a the amount of alcohol equivalent to the total free acid contained in one litre of wine, on the assumption that it is acetic acid (46 alcohol=60 acetic acid), y the proportion p.c. of a present as ester in one litre of wine when the alcoholic strength of the wine is A, and x be the amount of alcohol present in the compound ethers of one litre of wine; then

$$y=1{\cdot}17A+2{\cdot}8$$
$$x=\frac{y\times a}{100}$$

The alcohols other than ethyl alcohol present are left out of the account, but as they are insignificant in amount the error is trifling. This formula affords a mode of judging of the age and genuineness of wines, except in the case of very young wines, or wines which have been recently fortified, the esters in these cases being less than that required by the formula. The maximum esterification is reached in from 4 to 6 years. The alcohol obtained by the decomposition of all the esters rarely exceeds 0·06 p.c. of the wine. (For Thudichum and Dupré's method, *v. l.c.* 203.)

Sugar in wine. The sugars occurring in must and in wine are dextrose and lævulose. Cane sugar is never naturally present in must, but it is sometimes added, as in the case of champagne, but even then it is rapidly transformed into invert sugar. Glycerol is formed as a by-product of the growth of yeast during the process of fermentation, and is accompanied (amongst other changes) by the decomposition of sugar. For every 100 parts of sugar which disappear, from 3 to 4 parts of glycerol are produced. After complete fermentation the sugar seldom reaches 0·5 p.c., but when fermentation is arrested by the addition of alcohol, as in the liqueur wines of France and Spain made from dried grapes, and the sweet wines of Hungary, the sugar may be as much as 20 p.c. or more. In some wines—as *e.g.* Sauternes and sweet Rhine wines—sugar occurs in the form of inositol.

The colouring matters in wine are due to two sources. In white wines—which range from an almost colourless liquid, as champagne, to the deep yellow sherry—the colour is derived from the oxidation of the so-called extractives contained in the juice, which, as was before explained, is separated from the husks as quickly as possible. The grapes of some of the best red wines yield an almost colourless juice if pressed before fermentation, and it is only by the joint action of alcohol and acid upon the husks, stalks, and seeds during fermentation, that the red colour is extracted from the marc. Mulder separated the colouring matter contained in red wines by means of lead acetate, and found it to consist of a substance which was bluish-black in colour and amorphous in structure. It is only sparingly soluble in alcohol, insoluble in water, ether, chloroform, carbon disulphide, oil of turpentine, oil of olives; but soluble in solution of tartaric acid or cream of tartar, and in alcohol containing a trace of acetic acid, the saturated solution showing a blue colour; more acetic acid turns the solution red. It is soluble also in alcohol containing tartaric acid, exhibiting a red colour, but neither of these acids renders it soluble in ether or chloroform. The colour of wine, consequently, depends both upon the amount of colouring matter and the amount of free acid contained in it, as the violet colour becomes redder in proportion to the quantity of free acid acting upon the blue colouring matter.

The colouring matter precipitated by hydrochloric acid—in which it is deposited slowly at the ordinary temperature, but more rapidly on boiling—has been examined by Terreil (Bull. Soc. chim. [ii.] 44, 2). The precipitate always contains a substance resembling ulmic acid, from which the colouring principle may be dissolved out by alcohol. Thus obtained it forms brittle varnish-like scales, insoluble in water and ether, but readily soluble in alcohol, forming a brownish-red solution with a slightly yellow tinge. Acids change this colour to an intense red, while alkalis give a green colouration, which changes rapidly to a brownish-yellow on exposure to the air (*cf.* O. Griessmayer, Dingl. poly. J. 123, 531; Chem. Soc. Trans. 1887, 368).

The colouring matter of red wines (*œnolin* or *œnocyanin*) may be estimated with sufficient accuracy for technical purposes by the method of Cari Mantrand (Bull. Soc. chim. 1906, [iii.] 35, 1017), by precipitating with lead acetate, decomposing the precipitate with sulphuric acid, filtering, and weighing the residue from an evaporated portion of the filtrate. The œnocyanin may be concentrated and preserved in glycerol for use in confectionery, &c. The maximum amount found was 17·2 grms. per litre in Algerian wine.

Some additional colour is imparted to white wine by the tannin extracted from the oak casks during maturing. On the other hand, the natural colouring matter of red wine is reduced by the operation of fining as well as on ageing.

Caramel is frequently used to colour white wines (*e.g.* brown sherry), and occasionally boiled must is added either to the juice before fermentation or to the finished wine. (For foreign colouring matters, *see* below.)

Tannin is derived from the grape skins and stalks, the juice itself being practically free. It is sometimes added, however, to champagne and other white wines to prevent 'scuddiness' or turbidity. The natural tannin of grapes is decomposed by acids or by fermentation into glucose and an acid which is not gallic acid.

The *albuminous substances* in the grape, which set up the ferment, ought by that action to be removed in the yeast when the fermentation is properly carried out, and should not exceed 4 parts per 1000 of wine, unless the latter has been 'fined.' The albuminous matter is also reduced by 'plastering,' and in *old* wines it is thrown out together with tannin and colouring matter. In imperfectly fermented wines a certain amount remains, and, in the case of white wines, may again render them liable to fresh fermentation. In red wines this danger is obviated by the presence of the tannin of the husks, which preserves the albuminous matter from change.

The small quantity of *ammonia* which is present in grape juice, or is formed during fermentation out of albuminous substances, is, for the most part, precipitated during fermentation as magnesium-ammonium phosphate; a small amount, however, remains, and in some wines is accompanied by minute traces of trimethylamine.

Under the term '*extractives*,' some chemists include all matters other than water, alcohol, and volatile acids; others only those substances which are not volatile up to 100° or 110°. The latter would, however, exclude glycerol, which is properly included amongst the extractives. The composition of certain constituents of the extract which contribute to the smell and taste of the wine is still very obscure. The extractives are, of course, abnormally increased by plastering and addition of sugar (*v. infra*).

The *mineral constituents* of wine, as found in the ash, are potash, soda, and lime as phosphates, chlorides, carbonates, and sulphates, traces of iron, magnesia, and silica, and occasionally alumina, lithia, and manganese. In pure natural wines the ash rarely exceeds 0·3 p.c., but may be much higher in wines which have been plastered, or to which alkalis have been added to reduce their acidity.

As regards the amount of *alcohol*, a very comprehensive set of tables, embracing the results of the examination of 133 wines, is given by Thudichum and Dupré (Treatise on the Origin, Nature, and Varieties of Wine, 128–304), from which the following *resumé* is compiled:—

	Strength of wines in degree of proof spirit
German wines, 35 samples . .	16·2–26·3
French wines, 22 samples . .	18·0–37·2
Spanish wines, 22 samples . .	26·7–41·7
Sicilian wines, 6 samples . .	33·5–36·3
Portuguese wines, 14 samples . .	21·9–42·5
Hungarian wines, 10 samples . .	19·2–26·4
Greek wines, 8 samples . . .	17·8–32 1
Cape wines, 7 samples . . .	36·1–51·7
Atlantic Islands, 3 samples . .	38·2–39·1
Elba wines, 1 sample . . .	34·9
Australian wines, 5 samples . .	23·5–40·1

Sugar solution wines. Musts which are too thin, and deficient in sugar, are sometimes concentrated by evaporation (as in Portugal) or, more frequently, a solution of sugar is added. The latter process was first sanctioned by the French minister, Chaptal, and is known as 'Chaptalising.' A similar process (applied chiefly to acid musts), and known as 'Gallising,' from its inventor Gall, is also practised in Germany. The must of bad years, which contains a deficiency of sugar and an excess of acid, is mixed with sugar, preferably cane sugar, so as to bring the amount of sugar in the liquid to about 20 p.c., and to reduce the amount of acid to about 2 p.c. Frequently, however, commercial glucose is used, and its addition can frequently be detected in the finished product by its dextrorotatory polarisation.

The acidity of natural wine can also be

reduced, as suggested by Liebig, by the addition of neutral potassium tartrate, which throws down the free acid, if present as tartaric acid, as acid potassium tartrate. Wine deficient in alcohol and containing much acid may often be improved by adding to it the pressed residue of a succeeding vintage (*cf.* J. Nessler, Bied. Zentr. 1884).

A considerable quantity of wine is now made by covering the marc with an aqueous solution of sugar, and allowing the mixture to ferment. The sugar solution contains 18 grms. per litre for every degree of alcohol which it is desired to obtain, and 250 grms. of marc are used for each litre of solution. Analyses of wines prepared in this way by Girard, and of other samples found in commerce, prove that these wines have an approximately definite composition. When they contain from 9 to 10 degrees of alcohol, the proportion of soluble matter, cream of tartar, tannin, and colouring matter is much less than in the ordinary vintage wines. The amount of solid matter varies from 14 to 18 grms. per litre; the amount of cream of tartar is about 2 grms., but not less than 1·6 grm. per litre; whilst the proportion of tannin and colouring matter varies considerably with the nature of the marc. Girard concludes that those wines constitute a highly useful beverage, and can be produced at a very low cost (A. Girard, Compt. rend. 95, 227; Chem. Soc. Abstr. 1882, 1335).

Plastering of wine. The practice of adding gypsum or plaster of Paris to must, either before or after fermentation, which prevails in Spain, Portugal, and the South of France, is said to have for its object the reduction of the amount of the water in the juice, and the production, consequently, of a must relatively richer in sugar. The fermentation is much more rapid and complete, and it is alleged that the wine keeps longer when it has been plastered, and that the colour is richer and more lasting. This explanation leaves something to be desired, because the sacrifice of other constituents of juice than water by the absorption of plaster is entirely out of proportion to any gain by the absorption of the water, and the result desired could be attained either by the addition of sugar or the evaporation or freezing out of water. It is probable that the reason for the practice, although unknown to those who employ it, is that gypsum precipitates some albuminous matters which injuriously affect the wine. An obvious advantage to the wine-maker is that it clarifies the wine rapidly and so enables it to be brought sooner to market.

The plaster of Paris, in the form of powder, is either thrown upon the grapes before they are crushed, or added to the must after fermentation has commenced, or even to the finished wine, and the chemical changes that take place vary accordingly. The quantity used is generally from 1 to 2 kilos. to every 100 kilos. of fruit, although sometimes it reaches as much as 10 kilos.

According to Griessmayer, when gypsum is added to the must, it forms, with the tartar present, neutral calcium sulphate and free tartaric acid, which latter reacts on the sulphate, forming bitartrate and acid calcium sulphate. The ash of such wine is neutral, and does not give off carbon dioxide when treated with hydrochloric acid. When gypsum is added to the finished wine, the alcohol prevents its solution, but it carries down many impurities. Kayser (Bied. Zentr. 1881, 632) made experiments which confirmed these conclusions, and states that from the proportions of the ash to the extractive matter, it is possible to declare with certainty whether the wine has been plastered as must or as finished wine; in the first case the ash is disproportionately high, in the other it remains normal. Kayser also states that by the interaction of $KHSO_4$ and KH_2PO_4, free phosphoric acid is formed together with neutral potassium sulphate, the former producing the bright colour of plastered red wines. The main change, however, appears to be a decrease in the tartrates and an increase in the proportion of potash and sulphates.

The injurious effects attributed to plastered wines have been the subject of investigation by several commissions appointed by various foreign governments. The most exhaustive inquiry yet made on the hygienic aspect of the subject was by a commission appointed by the French War Department owing to complaints made by the French army in Algeria, where many cases of illness were said to be due to the use of plastered wines. The symptoms are said to be colic, and slight vomiting. The acid potassium tartrate acts towards many reagents in the same manner as free sulphuric acid, and when introduced into the system may have the effect of reducing the alkalinity of the blood.

In view of the inconclusive nature of the evidence, the Commission recommended the maintenance of the regulation forbidding the sale of wines containing more sulphate than that corresponding with 2 grms. of potassium sulphate in the litre, and this limit has been also adopted in Germany, Switzerland, and other countries.

The attempts to '*de-plaster*' wine are, from a hygienic point of view, more injurious than the plastering, owing to the use of poisonous barium and strontium salts.

Wine is liable to be affected by a number of injurious ferments, and is especially subject to acetous fermentation, due to ***Mycoderma aceti***, which principally attacks the alcohol with production of acetic acid, whilst ***Mycoderma vini*** attacks principally the cream of tartar and extractive matters. The action of foreign ferments may frequently be prevented by the process devised by Pasteur, which consists in heating the wine for some time to about 70° in absence of air. The bouquet, and in some cases the colour, is thus found to be improved. The heating must be quickly performed, and, as far as possible, out of contact with air.

Numerous substances are employed for the preservation of wine by chemical means as *abrastol* or *asaprol* (the calcium salt of β-naphthol sulphonic acid), *benzoic*, *boric*, and *cinnamic* acids, *fluorides*, *formaldehyde*, *saccharin*, *salicylic acid*, *sulphurous acid*, and *sulphites*. It should be noted that of these, boric acid, fluorine, and salicylic acid may be present in minute quantities as natural constituents of the wine (*v. infra*).

Manufacture of 'sparkling' wines. The effervescence of a sparkling wine is due to the presence of carbonic acid, produced by the fermentation of added sugar. The chief wines of this class (champagne) are produced in the departments of Marne and Haute Marne, and in the vicinity of the Moselle and the Rhine. Both white and red grapes are used, and the wine is amber in colour, the depth of tint depending on the vintage and the proportion of dark grapes employed. The vintage is in the early part of October, and in the pressing the must is separated into two portions, that first produced being of the higher quality. The young wine is allowed to ferment until the winter, when it is racked, and after the expiration of a month the operation is repeated, when the wine is fined. It is then mixed with a certain proportion of old wine, and the amount present determined. If necessary, a quantity of cane sugar is added, and the wine is bottled, the bottles being placed horizontally in piles and left at rest throughout the summer. Carbonic acid is formed, together with a quantity of sediment. The pressure of the gas in the bottles can readily be ascertained, when desired, by means of a manometer (such as Salleron's modification of Maumené's 'Aphrometre'), and ranges from 5 atmospheres in *grand mousseux* to less than 4½ in *crémant* wine; in ordinary mousseux wine the pressure varies between 4 and 4½ atmospheres. When required for the market, the bottles are first carefully brought into an inclined position, so as to cause the sedimentary matter to fall gradually on to the cork; on removing the clip which holds the cork within the neck the pressure of the dissolved gas forces out the cork, together with the sediment. A certain amount (from 1 to 4 p.c., depending upon the sweetness desired) of liqueur, made of fine wine, sugar, and cognac or a still spirit, is quickly added, and the bottles are again filled up, corked, and wired.

Dry champagnes—*i.e.* containing relatively little sugar—are mainly exported to this country, the sweeter varieties being usually consumed in America and on the Continent.

Wines of France. The chief wine-growing district in France is the Gironde, which is practically divided into five portions, viz., the Médoc, the Graves, the Côtes, the Palus, and the Entre-deux-Mers. In the Médoc some six or seven different varieties of vine are cultivated.

Most of the *red wine* is obtained from the Carbenet Sauvignon, Franc Carbenet, Malbec, and Merlot grapes. The vintage usually begins towards the end of September, and lasts about a fortnight. The wines (usually known as 'clarets') are divided into *paysan, artisan, bourgeois,* and *fine growths,* the last group being further sub-divided into what are known as 'crus' or 'classed growths,' named after the place (Château or Commune) where they are produced; *e.g. Château Latour, Pauillac*; *Château Lagrange, St. Julien*; *Château Margaux*; *Château Cantenac,* &c.

The chief *white wine* producing district is to the south of Bordeaux. The principal vines are the Semillon, Sauvignon, and Muscatelle. The vintage is much later than in the Médoc—viz. in the last weeks of October or early part of November, when the grapes have entirely ripened. Three qualities of must are produced: the first and ripest juice yields a sweet luscious wine (*vin de tête*), mainly consumed in Russia; the second forms *vin de milieu,* the wine usually known as *Sauterne*; the third quality, or *queue,* yields a dry white wine. The principal varieties are *Barsac, Sauterne, Graves,* and *Bommes, Château Latour-blanche,* and *Château Y'quem.*

The department of the Pyrénées Orientales produces a considerable quantity of wine, mostly from the Grenache noir and Carignane grapes. The generic name of the wine of the district is *Roussillon,* of which the most esteemed varieties are muscat of *Rivesaltes, Maccabeo, Malvoisie,* and *Grenache,* which are liqueur wines (the last-mentioned being simply unfermented must preserved by means of added spirit and sulphurous acid, with frequent racking from deposits); and *Rancios,* dry *Malvoisie,* and *Picfoule.* Languedoc also produces a large quantity of wine (*vins du Midi*), much of which is mixed with the wines of the Gironde and of Burgundy; whilst a considerable amount of the rest is distilled to make 'trois-six' and *eau de vie.* Cognac is produced from the wines of the Charente district (*v.* Brandy).

The Rhône and Saône valleys produce the chief wines of the east of France, which, with the exception of *Hermitage* and the wines of the *Beaujolais,* seldom occur in trade under their own names.

The best qualities of *champagne* (*v. supra, Sparkling wines*) are produced in the departments of Marne and Haute-Marne, the chief centres of the trade being at Rheims, Épernay, Aÿ, Avize, Châlons, and Dizy. The most famous brands are *Ayala, Cliquot, Heidsieck, Irroy, Moët, Mumm, Perrier Jouët, Pommery-Greno, Roederer,* and *St. Marceaux.* Large quantities of sparkling wine are produced in the Saumur, in the department of Maine-et-Loire. Sparkling *Saumur* is made from both black and white grapes—the black being the product of the Breton vine, the white that of the Pineau blanc. The wine is made much in the same way as champagne, except that, as a rule, the finished product is a mixture of two successive vintages.

The wines of *Burgundy* (both red and white) are produced in the departments of Côte-d'Or, Yonne, and Saône-et-Loire. The principal *red* wines are *Mâcon, Beaune, Le Corton, Romanée Conti, Chambertin* and *Clos Vougeot. Hermitage,* when it can be obtained genuine, is a rich wine with purple colour, produced in the department of Drôme. The *white* wine of Yonne is known as *Chablis.*

Spain. *Sherry,* the best known of Spanish white wines, is mainly produced in Andalusia, and derives its name from Jerez or Xeres de la Frontera, the chief centre of the trade, and where most of the wine is produced from must or fruit purchased from the growers. Sherries are usually broadly classed as *Amontillados* and *Manzanillas.* The former are usually deeper in colour and more alcoholic from added spirit; the latter are lighter and drier, and are, as a rule, shipped unbrandied. *Montilla* produced in the province of Cordova somewhat resembles Manzanilla. Sherries are almost invariably fortified and plastered, and the commoner kinds sulphured in addition, for the British market. The sweet red wine known as '*tent*,' which is used for ecclesiastical purposes, is mainly obtained from the Rota district. This and the somewhat similar wines from the Tarragona, Valencia, and

Alicante districts are frequently sold under the name of 'Spanish port.'

Portugal. Port is mainly the produce of the rugged and mountainous district of the Alto Douro in the north-east of Portugal. The vintage usually begins at the end of September. The grapes, from which the stalks are removed, are emptied into stone tanks holding from seven to thirty pipes, and are pressed, first by treading and then by means of a beam or screw press. After from 48 to 60 hours' treading the must is left to ferment, drawn off into vats, and mixed with a sufficient quantity of alcohol to prevent acetous fermentation. After the lees are deposited the wine is again racked and mixed with more alcohol, which is usually obtained by distilling wine. If necessary, the wine is sweetened with 'jeropica,' or sweet must preserved with brandy. In the spring it is sent down to Oporto, where it is stored previous to shipment. 'Vintage wines' are those of the same origin, year, and quality, and are kept separately, whilst 'factory ports,' which constitute the bulk of the wine exported are a mixture of wines of different year and origin. Nearly half the wine exported from Oporto is sent to the United Kingdom.

Port first appeared in England at about the end of the seventeenth century, and its consumption in this country gradually increased up to the middle of the eighteenth century, since when it has gradually declined.

The South of Portugal (Torres Vedras and Collares) produces a considerable quantity of a rough kind of claret, and also a white wine known in England as Bucellas Hock, which is obtained from the Riesling grape.

Italy. It is only within recent years that Italian wines have found much favour in this country. Northern Italy produces *Montferrat* and *Asti*, together with a certain amount of sparkling wine. *Montepulciano* and *Chianti* are made in Central Italy; whilst the Neapolitan district yields *Lacryma Christi* and a variety of Malvoisie and good class Muscat wines.

Sicily. The chief Sicilian wine is Marsala (a white wine of light amber or brown colour, somewhat resembling sherry), obtained from a mixture of selected and thoroughly ripe grapes of the Madeira variety. It is carefully manufactured and is very uniform in quality, although, as a rule, somewhat heavily fortified, but not plastered.

Austro-Hungary. Both white and red wines are made, but those of German Austria are consumed for the most part locally. The best known are from Vöslau and Gumpolds-Kirchen, and the Tyrol. The most famous of Hungarian wines is the Sweet Tokay or Essentia, which is made from the first runnings of the ripe grapes obtained without pressure. Only a small portion is so obtained, and it rarely, if ever, appears in the market. Other varieties of Tokay are known as *Ausbruch* and *Mástás*. *Carlowitz* resembles port in character, and is produced on the banks of the Danube, about 40 miles to the north-west of Belgrade.

Excellent red wines, resembling Burgundy, are now made in Dalmatia. The most esteemed varieties are *Moscato Roso*, *Maraschino*, and *Malvasia*.

Germany. The chief wine-producing districts of Germany are Alsace-Lorraine, Baden, Bavaria, Hesse, the Rheingau, and Wurtemberg. The celebrated *Steinberg*, *Johannisberg*, *Rüdesheim*, *Gräfenberg*, and *Rauenthal* wines are produced in the neighbourhood of the Rhine, not far from Mainz, which is the centre of the hock trade. The vineyards of Hesse yield *Liebfraumilch*, *Nierstein*, and *Scharlachberg*; *Hochheimer* is obtained from the Maingau. The chief Rhine vine is the Riesling, which is said to be indigenous, and which has been transplanted and successfully cultivated in many other parts of the world as South Africa, Australia, and the United States of America. The *Moselle* district also produces excellent wines of characteristic but rather weak flavour, which is often artificially enhanced by the addition of tincture of elder flowers.

The chief product is a white wine. A certain amount of red wine is obtained, notably Assmannshausen, from Riesling and mixed grapes. The results of analyses by König of wines from the principal European countries are shown in the table on next page.

The Atlantic Isles. Grand Canary and Teneriffe produce a small quantity of wine, but since the production of cochineal has fallen off on account of the preference for coal-tar colouring matters, vine culture is increasing, and wines of the Madeira type are being made in larger quantity.

Madeira. The best-known varieties of Madeira wine are *Malmsey*, *Sercial*, *Bual*, and *Tinta*. It is a white wine, usually dry (*i.e.* free from sugar), and its characteristic flavour is probably due to the practice of heating the wine shortly after its manufacture to a temperature varying from 25° to 45°. Formerly the same condition was obtained by sending the wine a voyage to the East or West Indies and back. Very little red wine is made in Madeira.

A small quantity of wine is made in the Azores, particularly on Pico, but it is of very indifferent quality, and is mainly exported as low-class sherry.

Cape of Good Hope. Comparatively little wine is now sent to this country from South Africa, although a century ago the importation of Cape wine into the United Kingdom exceeded that from France. The decline is due to vine diseases and insect pests, to faulty manufacture, and to fiscal changes. The best-known wines are *Drakenstein* or *Cape Hock* from **Paarl**; the sweet pale-red *Constantias* produced near Cape Town; and *Hermitage*, a red wine of Burgundy charcter.

Australia. Of late years the amount of wine from Victoria, New South Wales, and South Australia imported into this country has increased enormously. The industry may be said to be still in its infancy, but the most scientific methods and appliances are adopted, and the produce of such vineyards as Albury, Great Western, Highercombe, and Tintara bids fair to rival the best European wines of similar type.

United States. The manufacture of wine is now firmly established in California. The produce was originally derived from the 'Mission' grape, supposed to have been imported from Mexico by Franciscan monks, but German, French, and Spanish varieties have now been introduced, and wines in some degree resembling

Analyses of European Wines (König).

—	Number of Analyses	Specific gravity	Grammes per 100 c.c.									
			Alcohol by weight	Extract	Total acid as tartaric	Free tartaric acid	Cream of tartar	Volatile acid as acetic	Sugar	Glycerol	Nitrogen	Ash
Germany:												
Moselle . . .	14	0·9964	7·99	2·24	0·79	—	—	—	0·03	0·72	—	0·175
Rhine . . .	23	1·0005	8·00	2·60	0·81	—	0·200	—	—	0·85	—	0·230
Baden . . .	46	—	6·65	2·16	0·91	0·018	0·358	—	0·09	0·49	—	0·207
Wurtemburg, white wine	15	0·9995	6·10	2·27	0·95	0·095	0·262	—	—	0·57	—	0·250
„ red wine .	6	—	4·73	2·64	1·14	0·091	0·026	—	—	0·46	—	0·250
Alsace . . .	15	—	6·59	2·07	0·70	0·018	0·168	0·052	—	0·55	0·028	0·229
Lorraine, red wine .	10	0·9967	8·08	2·27	0·56	0·032	—	0·155	0·09	0·50	0·019	0·185
France:												
Red wine . . .	29	0·9982	7·80	2·56	0·57	—	—	—	0·30	0·73	0·043	0·248
White wine . . .	5	0·9963	8·30	3·03	0·66	—	—	—	—	0·97	—	0·250
Austria:												
Tyrol, red wine . .	60	0·9940	9·08	2·34	0·62	—	—	—	—	0·65	0·021	0·222
„ white wine .	17	0·9927	8·84	1·87	0·59	—	—	—	—	0·65	0·020	0·175
Russia:												
Red wine . . .	10	0·9939	10·76	2·76	0·56	—	—	0·142	—	0·64	0·036	0·267
White wine . .	12	0·9931	11·96	2·57	0·49	—	—	0·100	0·46	0·59	0·026	0·204
Italy . . .	20	—	10·61	3·44	0·52	—	—	—	1·44	0·45	—	0·290
Spain:												
Ordinary red wine .	7	—	12·30	3·53	0·49	—	—	—	0·38	1·09	—	0·610
Sweet wine . . .	4	1·0233	12·78	9·69	0·59	—	—	—	6·55	0·63	—	0·740

those of these countries (and named after their original types) are now made on a considerable scale. The vine is also cultivated on a large scale in Ohio, and clarets and champagnes are made in the vicinity of Cleveland and Sandusky. Other wine-producing States are New York, Missouri, Illinois, and Pennsylvania. Whilst the finer wines consumed in the United States are still obtained from France and Germany, the importation of foreign wines is steadily decreasing in favour of the home product.

The following are analyses, by Bigelow (U.S. Dept. of Agric. Bur. of Chem. Bull. 59), of 525 samples of wines manufactured in California:—

Description		Specific gravity	Alcohol by volume p.c.	Grams per 100 c.c.							
				Alcohol	Glycerol	Total acids	Extract	Reducing sugar	Proteids	K_2SO_4	Ash
Red wines (204 samples):											
Bordeaux, Rhine, Burgundy and South French types	Min.	0·9900	8·00	6·35	0·330	0·201	1·91	0·030	0·1864	0·0455	0·188
	Max.	1·0050	19·28	15·30	0·852	0·888	6·88	0·628	0·5544	0·2515	0·430
White wines (321 samples):											
Rhine, Sauterne, South French, Sherry and Madeira types	Min.	0·9866	5·00	3·98	0·163	0·181	1·09	0·060	0·0859	0·0453	0·050
	Max.	1·0560	22·19	17·61	0·971	0·798	19·66	17·210	0·9379	0·1861	0·447

ANALYSIS OF WINE.

The chemical examination of wine is usually restricted to the determination of those constituents which enable an opinion to be formed concerning its purity or freedom from adulteration, but expert tasting is of great importance, and microscopical examination of the deposits obtained from wine may afford useful information.

For the estimation of the *specific gravity* a determination should be made by the bottle or other form of pyknometer and given accurately to four decimal places. Carbonic acid should first be removed by vigorous agitation.

The *results* are usually given in grms. per 100 c.c. or per litre. Koenig (Zeitsch. anal. Chem. 28, 202), however, deprecates this practice, on the ground that for sweet wines, which are liable to differ widely in sp.gr., the results are no longer directly comparable.

The *alcohol* is best determined by the distillation method, the sp.gr. of the weighed distillate being taken and the proportion of alcohol found from tables. For more exact determinations, the volatile acids should be neutralised before distillation.

Determination of extract. The various methods in use for determining extractive matter in wine differ considerably both in principle and in the details of manipulation. The direct method (by evaporation) does not give comparable results unless the sugar of sweet wines and the potassium sulphate in plastered wines are deducted, and not then unless the estimation is conducted under exactly similar conditions.

The French official method of prolonged heating on a water-bath gives low results, owing chiefly to loss of glycerol. The sugar and potassium sulphate are deducted, an allowance of 1 grm. of each per litre being made to cover the amount of these substances assumed to be naturally present in fully fermented wine. The result is known as the 'reduced extract.'

The most exact determination of extract is made by evaporation (at the ordinary temperature) over sulphuric acid *in vacuó*, but as this requires from 3 to 6 days (according to the temperature) it is unsuitable for ordinary commercial use.

The German official method is as follows :—

(*a*) For wines with an extract amounting to not more than 3 grms. per 100 c.c. (ascertained by the indirect method (*c*) given below): 50 c.c., measured at 15°, are evaporated to a syrupy consistency on the water-bath in a platinum basin of 85 mm. diameter, 20 mm. height, and 75 c.c. capacity, and the residue is dried for 2½ hours in the water oven.

(*b*) For wines containing from 3 to 4 grms. of extract per 100 c.c. an amount yielding from 1 to 1·5 grm. of residue is taken. For the necessity of using dishes of similar area and surface in order to obtain comparable results, *v.* Bouilhon (Compt. rend. 103, 498).

(*c*) For sweet wines, or those containing over 4 grms. of extract per 100 c.c., the indirect method of determining the extract from the sp.gr. of the wine after removal of the alcohol is to be preferred (*v.* Tables in Windisch, Die Chemische Untersuchung und Beurtheilung des Weines, 338; abstracted, J. Soc. Chem. Ind. 1898, 280).

The amount both of extract and of alcohol may be determined by Riegler's refractometer method (Zeitsch. anal. Chem. 1896, 27). One grm. of alcohol and of extract in 100 c.c. of wine are found to raise the refraction by 0·00068 and 0·00145 respectively above that of water. Then if a=the refraction of pure distilled water; $(a+b)$=the refraction of the wine from which the alcohol has been removed made up to the original volume taken; and N=the refraction of the original wine; then the formula $\frac{N-(a+b)}{0{\cdot}00068}$ gives the weight of alcohol, and $\frac{b}{0{\cdot}00145}$ that of the extract as grams per 100 c.c. of the wine.

In completely fermented wines the amount of extract is seldom less than 14 grms. per litre. Wines containing less than this amount after removal of the sugar may be suspected of dilution.

After separation of the non-volatile acids, the remaining extract in natural wine is seldom less than 11 grms. per litre, and after separation of the free acids, as a rule, not less than 10 grms. per litre. The mineral constituents are usually about 10 p.c. of the extract.

The *free acid* is determined by titration with standard potash or soda-solution, using litmus-paper as indicator, and calculating the result as tartaric acid ($C_4H_6O_6$). Carbonic acid should first be expelled, either by heating just below boiling-point (but rapidly so as to avoid loss of acetic acid), or by agitation and subsequent titration in the cold. *Volatile acids* are determined by distillation in steam, or, since this partially volatilises lactic acid (Windisch, Zeitsch. Nahr. Genussm. 1905, 9, 70), by the difference in the acidity of the wine before and after evaporation to a small bulk, and are expressed as acetic acid ($C_2H_4O_2$). The *fixed acids* are estimated by difference between the total and volatile acids, or by direct titration of the extract obtained by evaporation *in vacuô*, and are expressed as tartaric acid. In France the acidity is usually given in terms of sulphuric acid (H_2SO_4).

Old wines have an acid reaction, in consequence of the presence of a certain amount of free acid and potassum hydrogen tartrate. A wine not exhibiting this acid reaction tastes flat. For a long time it was believed that the free acid of wine is tartaric acid alone. Nessler's researches have, however, shown that this is seldom the case. Tartaric and malic acids often exist together, and more frequently the free acids consist of malic acid entirely. Wines containing tartaric acid alone taste more tart than those with only malic acid, or a mixture of malic and tartaric acids.

The presence of free tartaric acid in wine does not necessarily show an improper admixture of tartaric acid with the wine. According to Mach and Rolondi, the amount of free tartaric acid in the grape increases in proportion to the degree of unripeness, so that its absence from wine can only occur under certain conditions of ripeness of the grapes employed. Although unripe grapes are frequently used in considerable quantity in wine-making, yet if the ripe grapes are in excess, the potash salts in them are more than sufficient to separate the free tartaric acid in the form of tartar, and this explains the fact that wine so made generally contains no free tartaric acid. A wine may be suspected of having been sophisticated if, with a small amount of free acid, an undue proportion of it is tartaric (J. Nessler and H. Wachter, Bied. Zentr. 1880; Chem. Soc. Abstr. 1880, 775).

The estimation of *total tartaric acid, free tartaric acid, potassium bi-tartrate,* and *tartrates of the alkaline earths* (lime and magnesia) is best made by the methods of Halenke and Möslinger, and of Barth (Zeitsch. anal. Chem. 1895, 279–290). These methods were officially adopted by a German Imperial Decree of 1896, an abstract of which is given in the J. Soc. Chem. Ind. 1898, 277. Certain modifications were introduced by Kulisch in 1901. Full details of these, as well as the French official methods, will be found in Post and Neumann's Traité complet d'analyse chimique appliquée aux essais industrielle, 1910, tome ii. 661. The last three estimations are necessarily empirical, being founded on the assumption that all the bases present in the organic salts of the wine, or as carbonates in the ash, were originally combined with tartaric acid to form bi-tartrates.

Numerous methods have been suggested for the estimation of *malic* and *succinic* acids, but they are too uncertain and inexact to be of much value for analytical purposes. The methods for *lactic* and *citric* acids are more reliable, and the estimation of these is more important, since the former is a constant constituent of wines, and is often the cause of their excessive acidity, whilst the latter is rarely present in genuine wines, except in slight traces, but is sometimes added to sophisticated wines.

The best methods for estimating *lactic acid* are those of Kunz (Zeitsch. Nahr. Genussm. 1901. 4, 673) and Möslinger (*ibid.* 1901, 4, 1123). *Citric acid* may be estimated by Möslinger's method, weighing as lead citrate, as officially adopted by the U.S. Dept. of Agriculture (Bur. of Chem. Bull. 107, 81).

The determination of *glycerol* in wine has given rise to numerous processes, the best known of which are based upon either extraction by means of alcohol and ether and weighing, or oxidation to and estimation as oxalic acid.

Various methods have been proposed as steam-distillation under reduced pressure (Bordas and Raczkowski, Compt. rend. 1897, 124, 240); or by conversion into triacetin (Böttinger, Chem. Zeit. 1897, 659); or into *iso*propyl iodide and weighing as silver iodide (Zeisel and Fanto, Zeitsch. anal. Chem. 1903, 549). A method by Rothenfusser, claimed to be more rapid and less laborious and expensive than the official method described below, is given in Zeitsch. Nahr. Genussm. 1912, 23, 332.

The older methods, especially extraction with alcohol and ether, are generally preferred, since, although somewhat empirical, they yield results which are comparable with the enormous amount of similar data acquired by previous observers. It is essential, however, that the exact details of the given methods should be rigidly followed.

The method officially adopted in Germany is as follows, (*a*) being adopted in the case of dry wines or those containing less than 2 grms. of sugar per 100 c.c.; and (*b*) for sweet wines containing more than this proportion of sugar.

(*a*) 100 c.c. of wine is evaporated down to 10 c.c. in a porcelain capsule on a water-bath. 1 grm. of quartz sand is added and milk of lime (40 p.c.) equivalent to 1½–2 grms. CaH_2O_2 for each gram of extract present, and evaporation continued almost to dryness. The residue is then repeatedly boiled with small quantities of 96 p.c. alcohol, the various extracts being decanted into a 100 c.c. flask, made up to bulk at 15°, filtered, and 90 c.c. of the filtrate evaporated in a porcelain capsule on the water-bath (without boiling). The residue is washed into a stoppered graduated cylinder with small quantities of absolute alcohol until 15 c.c. are collected, then shaken up with three successive portions of ether (7·5 c.c. each time), and, when clear, the whole (including the rinsings of the cylinder with alcohol-ether, 2 : 3) evaporated on the water-bath to a syrup, but without boiling. The residue is dried for 1 hour at 100°, cooled, and weighed. The weight in grams, multiplied by 1·111, gives the number of grams of glycerol in 100 c.c. of the wine.

(*b*) 50 c.c. of wine are heated on the water-bath in a large flask, 1 grm. of quartz sand added, also milk of lime until the dark colour at first produced disappears, and an alkaline odour becomes evident. After cooling, 100 c.c. of 96 p.c. alcohol are added, the precipitate filtered off and washed with alcohol. The filtrate is evaporated and treated as in (*a*). The factor 2·222 is necessary in this case to obtain the number of grams of glycerol in 100 c.c. of the wine.

The *sugar* in wine is a variable mixture of dextrose and lævulose, and occasionally sucrose. The usual method of examination consists in estimating the total quantity of sugar by titration with copper solution, then ascertaining by the optical method the proportions of the two glucoses and estimating the sucrose after inversion with hydrochloric acid.

Valuable information as to the nature and proportions of the sugars (both natural and added), as well as of other optically active substances introduced for the purpose of sophistication, may be obtained by the use of the polarimeter. Pure wine which still contains unfermented sugars turns the plane of polarisation to the left, whilst perfectly fermented wine either does not polarise at all, or only very slightly to the right. Wines sweetened with commercial glucose may contain considerable proportions of dextrorotatory non-fermentable substances.

It is essential to remove alcohol and colouring matters, and Nessler and Barth show that it is a matter of considerable importance also to remove the tartaric acid present in the wine, and they add, before precipitating with alcohol, a few drops of a strong solution of potassium acetate, thus separating the tartaric acid as potassium hydrogen tartrate.

The wine is carefully neutralised, and the alcohol eliminated by evaporation, the residue filtered, if necessary, and made up to original bulk, decolorised with lead acetate, the excess of lead removed with sodium carbonate or sulphate, and the polarimeter reading corrected for the increased volume due to these additions. The use of bone black should be avoided if possible, and complete decolorisation is not necessary if the liquid is clear. Turbidity can be removed by the addition of alumina cream.

A complete scheme, based upon the German official methods (Veröffentl. d. Kaiserl. Gesundheitsamts, 1896, 20, 557) is given in Allen's Commercial Organic Analysis, 1909, vol. i. 171. The results are obtained from observations in a 200 mm. tube, and expressed in terms of the sugar scale of the Schmidt and Hœnsch half-shadow saccharimeter.

For the estimation of sugar by Fehling's solution, the tannin must first be removed by lead acetate, the excess of lead being precipitated by sodium carbonate or sulphate. Ordinary fully fermented wine usually contains under 0·1 p.c. sugar, and may be decolorised by a small quantity of animal charcoal. Either the gravimetric method (weighing the precipitated copper as CuO) or the volumetric (using as indicator either potassium ferrocyanide or ferrous thiocyanate as recommended by Ling (Analyst, 1905, 182; 1908, 160) may be used.

Sucrose may be determined by difference between the directly reducing sugars formed as just described, and the total reducing sugar after inversion with hydrochloric acid on the water-bath, deducting one-twentieth of the difference (invert sugar) thus found to obtain its equivalent as sucrose; or the Clerget polariscopic method may be employed, using Herzfeld's modification of the Clerget formula (*v.* art. SUGAR).

Gum arabic and *dextrin*, which are sometimes used for sophisticating wines, may be detected by adding to a little of the wine about twice its bulk of the strongest alcohol. If a decided flocculent and viscous precipitate be formed, the gum is obtained by evaporating 100 c.c. of the wine to about 5 c.c., and precipitating by the gradual addition of 90 p.c. alcohol. The precipitate is filtered off, dissolved in about 30 c.c. of water, 1 c.c. of strong hydrochloric acid added, and the liquid heated in a flask provided with a long glass tube as a reflux condenser for 3 hours on a bath of boiling water. The sugar thus produced is then estimated in the usual manner by Fehling's solution.

Tannin. There is no very exact method for the estimation of tannin in wine. That of

Neubauer-Lowenthal is recommended, and is described, with modifications, by Fresenius and Borgmann in 'Analyse des Weines,' p. 99.

Mineral matter is found by cautious incineration of the residue from the evaporation of 50 c.c. of the wine, taking the usual precautions for separation of carbon from the alkaline salts. Rapid weighing is essential owing to the hygroscopic nature of potassium carbonate.

The determination of the ash (and of several other constituents) of wine containing much sugar is often facilitated and made more exact by eliminating the alcohol and removing the sugar by fermentation.

Wine containing less than 1·3 mineral matter per litre may be suspected unless it can be shown that natural wine from the same district and of the same vintage actually contains so small an amount of inorganic matter. The ratio of mineral matter to extract is, as a rule, about 1 to 10.

Estimation of chlorine in wine. It is well known to wine falsifiers that chemists lay much stress on the proportion of mineral matters contained in wine, and therefore they frequently add sodium chloride to artificial or adulterated wines in order to increase the extract and to bring the total amount of ash up to the normal quantity. It is also said to hasten clarification and to have a preservative effect. Owing to the volatility of sodium and calcium chlorides on incineration, chlorine is best determined in the wine itself and not in the ash, but the ordinary method of titration is inapplicable owing to the solubility of silver chromate in the free acid of the wine. The chlorine is either precipitated and weighed as silver chloride, or the method of Nessler and Barth may be employed as follows:—50 c.c. of the decolorised wine are acidified with nitric acid, an excess of standard silver solution is added, and then standard thiocyanate solution is run in until a drop of the liquid when mixed on a plate with ferric sulphate solution just shows a pink coloration.

Wines containing more than 0·05 p.c. sodium chloride may as a rule be suspected. Exceptions may occur in the case of wines which have been produced in the neighbourhood of the sea-shore.

Alkaline earths in wine. The ash of wine always contains calcium and magnesium salts. The amount of calcium (3–11·4 mg. in 100 c.c. of wine) is greatest in young wines and gradually diminishes with age, probably in consequence of the separation of neutral calcium tartrate. The amount of magnesium, on the other hand, remains almost constant and is always in excess of the calcium. The largest amount of magnesium found by Kayser was 24 mg. in 100 c.c. of Malaga wine. The phosphoric acid and magnesia show a constant proportion of 10 : 6, corresponding with the formula $MgHPO_4$ (Kayser, Chem. Zentr. 1881, 394; Chem. Soc. Abstr. 1882, 121).

Barium and *strontium* salts are sometimes added, to remove sulphuric acid, in the process of 'deplastering' wines, and are best detected in the ash, which should be taken up with dilute hydrochloric acid, filtered, and the filtrate evaporated to dryness. The dry residue is then examined by the spectroscope. If barium or strontium is present they are determined quantitatively in the usual manner.

Sulphuric acid is precipitated directly with barium chloride in wine acidified with hydrochloric acid, and determined in the ordinary manner.

A normal wine contains not more than 1·3 grm. K_2SO_4 per litre, and when the amount exceeds 2 grms., the wine may be regarded as plastered or sulphured.

The determination of *phosphoric acid* is to be effected in the ash by the molybdic method. (For details, *see* J. Soc. Chem. Ind. 1898, 280.)

The addition of dicalcium phosphate is sometimes made instead of 'plaster,' and is said to have certain advantages over the use of gypsum.

Nitric acid is sought for by carefully adding a few c.c. of the wine to a solution of diphenylamine in (pure) concentrated sulphuric acid, without mixing, and avoiding rise in temperature. An intense blue colour at the junction of the liquids indicates the presence of nitric acid.

Fresenius (Zeitsch. anal. Chem. 28, 67) finds that in wines containing much sugar a loss of phosphoric acid takes place during the incineration of the residue. A higher result is obtained when the residue is deflagrated with alkaline carbonate and nitrate. Destruction of the sugar by fermentation by addition of a very small quantity of yeast leads to the same result.

The assumption that the better kinds of wine always contain more phosphoric acid than the poorer ones is unfounded. At the same time the amount of the phosphoric acid can, in many cases, serve as a valuable means of ascertaining the character of a wine, especially of wines used for medical purposes, or of those of a particular district in which the amount of phosphoric acid varies between definite limits.

Examination for colouring matters. The principal substances used in red wines are vegetable colouring matters, coal-tar colours (especially fuchsines), and cochineal. White wines are frequently coloured with caramel or coal-tar colours used as substitutes.

According to Jean and Frabot (Ann. Chim. anal. 1907, 12, 52), wines artificially coloured may be distinguished from natural wines by the following test. The wine (50 c.c.) is heated on a water-bath with a little formalin (1 c.c.) and hydrochloric acid (4 c.c.), and when a precipitate is formed the liquid is made alkaline with ammonia and the excess expelled by further heating. The liquid, on cooling and filtration, yields a colourless filtrate in the case of genuine wines, whilst artificially coloured wines yield a coloured filtrate.

(*a*) *Vegetable colours.* These are derived chiefly from bilberries, black cherries, elderberries, hollyhock or rose-mallow, poke-berries (*Phytolacca*), indigo and lichens (archil, &c.), alkanet root, Campeachy, Pernambuco, and other dye-woods.

The wine is mixed with an excess of lead acetate and filtered. The colour of the precipitate in a genuine red wine may be greyish-blue, bluish-grey, ash colour, or greenish. If a precipitate is obtained not greatly differing from these colours, the search for other vegetable pigments can give no certain result. The colouring matter of *bilberries* gives a blue precipitate; *mallow* and *elderberries* a green. The colour of *Phytolacca berries* differs from that of red wine by giving a red-violet lead precipitate (*see* also Lenz, Zeitsch. anal. Chem. 1895, 635).

Alkanna-red, which, with Dupré's test (*v. infra*), behaves very like the natural colouring matter of wine, is very easily taken up from its solutions by amyl alcohol. On adding to the amyl alcohol a solution of a few drops of olive oil or oil of almonds and evaporating off the alcohol, the oily residue (after washing with water) has a fine red colour, which, on saponification becomes a rich blue, or if the alkanna used was old, a green (Herz, Zeitsch. anal. Chem. 23, 637; Chem. Soc. Abstr. 1890, 311).

Beetroot juice is used in colouring wines for the purpose of concealing the presence of magenta. The absorption-bands of magenta are hidden by those of beetroot, but if a few drops of copper sulphate solution are added to the wine, the beetroot bands gradually vanish and the magenta spectrum becomes visible.

The fresh colouring matters of *bilberries* and wines are similar but not identical, and, according to H. W. Vogel (Ber. 21, 1746), they are readily distinguished by their absorption spectra after careful neutralisation with ammonia, or, better still, when they are treated with a trace of alum before addition of ammonia. Care must be taken that the wine is not too concentrated or the ammonia in too great excess.

Detection of logwood in wine. When a solution of logwood is treated with manganese dioxide it becomes brown, and this brown liquid, by the action of zinc and hydrochloric acid, gives a colourless solution of hæmatoxylin. This may be detected by the ordinary reagents for that substance, alkalis and their carbonates giving a blue-violet colouration, calcium hydroxide a red-violet, stannous chloride or ammonium molybdate, in a solution slightly acid with nitric acid, a violet colouration. Advantage has been taken of this reaction for the detection of logwood in wines. 20 c.c. of the wine is agitated with 2 grms. finely powdered manganese dioxide, filtered, and the brown liquid treated with zinc and hydrochloric acid, which reduces the oxidised logwood colouring matter to hæmatoxylin. The solution is then divided into several portions, and tested with the reagents given above. Pizzi has examined wines to which other red colouring matters have been added, and although these yield brown solutions with manganese dioxide, the reduced solution does not give the hæmatoxylin reactions. Brazilwood is the only one which has any analogy to logwood, but here also there are differences (Chem. Soc. Abstr. 1881, 761).

Spaeth (Zeitsch. Nahr. Genussm. 1899, ii. 635; Analyst, 1900, 11) gives a table of reactions which may be found useful for the detection of the most commonly used vegetable colours.

(*b*) *Coal-tar colours.* In most cases the presence of a coal-tar colour in wine may be recognised by the following methods:—

a. By shaking the filtrate after precipitating with basic lead acetate with amyl alcohol, or (i.) the wine itself, also (ii.) a portion of the wine acidified with sulphuric acid, and (iii.) a portion made alkaline with ammonia. In the latter case, excess of ammonia should be avoided, as, if more than 3 p.c. the amyl alcohol may remain colourless, although the wine contains a coal-tar colour. The amyl alcohol extract in (i.) and (ii.) may contain natural colouring matter of the wine, but if the colour remain unchanged by ammonia, the presence of a coal-tar colour may be inferred. The amyl alcohol extract from (ii.) should be shaken up with water and the aqueous solution tested with ammonia or by the wool test.

b. By the wool test, using alum and sodium acetate as a mordant, and adding about 1 p.c. of potassium sulphate in solution.

c. By Cazeneuve's oxide test (Vierteljahrschrift für Chemie der Nahrungsmittel, 1886, 80; Compt. rend. 102, 52).

The oxides employed are yellow mercuric oxide in the proportion of 0·2 grm. per 10 c.c. of wine; lead hydroxide, containing 50 p.c. of water, in the proportion of 2 grms. per 10 c.c.; and gelatinous ferric hydroxide, containing 90 p.c. of water, in the proportion of 10 grms. per 10 c.c.

Mercuric oxide completely absorbs the natural colouring matter, cochineal and foreign vegetable colours, erythrosin, eosin J, methylene blue, Coupier's blue, and diphenylamine blue. It partially absorbs orange I., safranine, chrysoidine, chrysoine, methyleosin, yellow II., red NN, red I., and Ponceau RR. It does not absorb the sulpho-conjugated derivative of rosaniline, Bordeaux red B, Ponceau R, Ponceau B, orange R, orange RRR, orange II., orange RR, tropæoline M, tropæoline II., yellow I., solid yellow, dinitronaphthol yellow, U. S. yellow.

Lead hydroxide completely absorbs the natural colouring matter, cochineal and foreign vegetable colours, methylene blue, Coupier's blue, diphenylamine blue, and erythrosin. It differs from mercuric oxide in not absorbing the rosanilines, and also in absorbing the sulpho-conjugated derivative of rosaniline, Bordeaux red B, the purple red, and soluble red of rocelline.

Ferric hydroxide does not absorb erythrosin, the sulpho-conjugated derivative of rosaniline, Bordeaux red B, purple red, soluble red, and solid yellow. It absorbs the natural colouring matter and foreign vegetable colours, cochineal, and all the derivatives of rosaniline, except the sulpho-conjugated derivative.

Zinc hydroxides and stannous hydroxide behave similarly. The latter retains the natural colouring matter, but does not absorb cochineal or orchil. After the wine has been treated with the hydroxides, the colouring matters must be distinguished by special tests. If the wine is treated with magnesia and hot amyl alcohol, a number of blues which are precipitated by the above-mentioned hydroxides can be isolated and distinguished.

d. Shaking the wine with ether before and after supersaturation with ammonia.

Five to 6 c.c. of the wine to be tested are poured into a glass test-tube of about 20 c.c. capacity, and then three-quarters of its bulk of ether is added. After a few minutes the ether rises to the surface of the wine. If the ether be coloured yellow, and assumes, on addition of some drops of ammonia, a deep-red tint, Campeachy-wood has been used to colour the wine. If the ether becomes red and violet, and remains so even on addition of a large quantity of ammonia, the wine contains colouring matter derived from some of the lichens.

If the red-coloured ether loses its tint on mixing with ammonia, without passing into violet, then only the natural colouring matter of the wine, œnolin, is present. If the red-coloured ether loses its red tint with ammonia, without imparting any colour to the latter, then fuchsine has been added to the wine. When the ether rises uncoloured, a fresh sample of the wine to be tested is taken, twice its volume of water is poured into it, and half its volume of ammonia added. If the wine now assumes a brownish-red colour, it contains cochineal; if, however, it turns green, then it can be assumed that none of the substances mentioned is present.

e. The formation of *iso*nitriles when aniline derivatives are warmed with potash and chloroform serves for the direct determination in wine of even minute traces of many of the aniline colours. The evolution of the *iso*nitrile is accelerated by adding excess of strong sulphuric acid.

According to A. Dupré, fraudulent colouring matters added to red wines may be detected by dialysis, which is best accomplished by placing in the wine a cube of jelly about ¾-inch square. These cubes are made by dissolving 10 grms. of gelatin in 100 c.c. of warm water, and pouring the solution into a flat dish or mould; from the plate thus obtained the cubes are cut. After 24–48 hours the cube, on examination by transmitted light, will be found to be coloured more or less deeply by any colouring matter present, excepting the natural colouring matter, which penetrates only to a depth of ⅛-inch at the most. The colouring matter of alkanet root also penetrates but slowly, whereas rosaniline, cochineal, logwood, brazilwood, indigo, litmus, red cabbage, beet-root, *Malva sylvestris*, and *Althea officinalis* penetrate rapidly into jelly (Chem. Soc. Trans. 1880, 572).

The nature of the colouring matter may be determined either by the colour of the jelly or spectroscopically, or by the action of dilute ammonia, which turns cochineal purple, logwood brown, red cabbage dark green, and decolorises rosaniline (*v.* SPECTRUM ANALYSIS).

Bordeaux verdissant or 'colorant introuvable' is a mixture of acid fuchsine with methylene blue and diphenylamine orange, the two latter colours being used to produce a green which becomes visible on decolorising the Bordeaux red with ammonia, thus simulating the effect of ammonia on natural red wine. The diphenylamine orange can be extracted with amyl alcohol, the acid fuchsine detected by Girard's mercuric acetate test, and the methylene blue by dyeing cotton fibre.

A substance known as *Tintura por los vinos* is said to have been largely used for colouring certain Spanish wines. It contains Biebrich red, sodium sulphate, and arsenious oxide. The presence of arsenic is of special importance.

The methods employed in the Paris Municipal Laboratory for the investigation of the colouring matters in wine will be found in Girard and Dupré's 'Analyse des matières alimentaires.'

Detection and estimation of *preservatives* most commonly used in wine. *Abrastol* or *asaprol* (calcium α-monosulphonate of β-naphthol) is a white or slightly reddish scaly powder readily soluble in water and alcohol, and decomposing at 50°. It is extracted from alkaline solution by amyl alcohol, the extract evaporated to dryness, and the residue tested by Simibaldi's method (Mon. Sci. 1893, [iv.] 7, 842; U.S. Dept. of Agric. Bur. of Chem. Bul. 59, 91).

Boric acid (according to Baumert, Ber. 21. 3290) is naturally present in many wines as well as in the leaves and tendrils of the grape-vine. It is detected in the ash by extracting with a large excess of strong hydrochloric acid, and testing with turmeric paper. For its quantitative estimation, *see* Windisch, Die Chemische Untersuchung und Beurtheilung des Weines, 235.

Fluorides are strongly antiseptic and are usually employed in very small quantity in the form of the ammonium or sodium salts which are soluble in water. The fluorine is precipitated as calcium fluoride from alkaline solution by means of calcium chloride, and the precipitate, after filtering, washing, drying, and igniting in a platinum crucible, is tested by means of the 'etching' test. A blank experiment should be made with the reagents employed. For *fluoborates* and *fluosilicates* the ash containing the calcium salts is extracted with dilute acetic acid and filtered. The filtrate contains the boric acid which, if present, is detected as above. The calcium fluoride and silicate remain in the insoluble portion, and can be detected by the usual methods (*v.* Bull. 59, 63, U.S. Dept. of Agric. Bur. of Chem.).

For detecting *saccharin* (which is used as a preservative as well as a sweetening agent), the wine (about 100 c.c.) is shaken up with a mixture in equal parts of ether and light petroleum, and the extract, after evaporating off the solvent, is fused with sodium hydroxide and tested by means of ferric chloride for salicylic acid. It is assumed, of course, that the absence of salicylic acid in the original wine has been proved and the presence of saccharin indicated by the sweet taste of the residue from the ether extraction.

The estimation of the saccharin may be made by acidifying (if necessary) with phosphoric acid, extracting with ether as above, and fusing the evaporated residue with a mixture of sodium carbonate and nitre, precipitating the resulting sulphate with barium chloride and calculating the saccharin from the weight of barium sulphate obtained ($BaSO_4 \times 0{\cdot}785 =$ saccharin).

Saccharin may also be estimated by hydrolising the residue from the ether extract with hydrochloric acid, and estimating the ammonia thus formed by distillation into standard acid (Proctor, Chem. Soc. Trans. 1905, 242).

Salicylic acid is best sought for by agitating the wine with carbon disulphide or a mixture of equal volumes of ether and light petroleum (taking care to avoid an emulsion), evaporating down and testing the residue with ferric chloride. If much more than 100 c.c. are used, a faint colour may be occasioned by other substances giving a similar reaction and present as normal constituents of the wine.

An approximate estimation of the quantity of salicylic acid may be made colorometrically, by comparing the colour given by an alcoholic solution of the residue after ether extraction with that yielded by standard alcoholic solution of salicylic acid of known strength, using, if possible, a liquid similar to that under investigation.

Sulphurous acid and sulphites. Wine wi absorb as much as 0·36 grm. of sulphurous acid per litre when it is shaken in a barrel in which sulphur has been burnt, and if the treatment is repeated the sulphurous acid may reach 0·5 grm. per litre. Sulphur is burnt in the barrels to prevent the formation of mildew, and sulphites are sometimes used as a preservative. Much of the sulphurous acid is combined with aldehyde when it is considered to be much less objectionable than in the free state.

Sulphurous acid is determined by distilling a portion of the wine, to which phosphoric acid has been added, in a stream of carbon dioxide, receiving the distillate in solution of iodine, and determining the sulphuric acid thus formed. The details of the method are as follows (B. Haas, Ber. 15, 154): the wine, to which 5 grms. of syrupy phosphoric acid have been added, is distilled in a current of carbon dioxide, and the distillate is collected in a suitable apparatus (a bulbed U-tube) containing 50 c.c. of iodine solution, containing 5 grms. pure iodine and 7·5 grms. potassium iodide per litre, thus oxidising the sulphurous acid. As soon as the distillate amounts to about half the original volume of the wine used, the contents of the U-tube are washed out, acidified with hydrochloric acid, precipitated with barium chloride, and the barium sulphate washed, dried, heated to redness, and weighed. This method gives very good results.

Opinions vary as to how much sulphurous acid a wine may contain. According to the medical faculty of the University of Vienna, not more than 8 mg. per litre should be allowed, whereas other authorities regard 80 mg. as not an excessive amount. In France and Switzerland the maximum limit is fixed at 200 mg. of SO_2 per litre, of which, in France, not more than 30 mg., and in Switzerland, not more than 20 mg. should be 'free' or uncombined.

Poisonous metallic substances in wine. Traces of *arsenic* may be present owing to the use of impure coal-tar colours (acid fuchsine, &c.), and commercial glucose. *Copper* and *mercury* may be due to the compounds used as insecticides and fungicides, but are, no doubt, largely removed in an insoluble form during the process of fermentation. *Lead* has been traced to the use of litharge to mask acidity and to lead shot used for cleaning bottles. *Zinc* is often present in appreciable quantities when the wine has been stored in vessels of unalloyed zinc. These metals may be detected and estimated by the usual methods.

Alum is occasionally present in the coal-tar colours employed, and is sometimes added to wine as a clarifying agent, and to impart astringency, particularly to wines which have been diluted. The alumina may be estimated as follows (Louvet, Chem. Zentr. 1881, 252): 200 c.c. of wine are evaporated to dryness, the residue incinerated, and the ash fused in a platinum crucible with 3 grms. sodium carbonate, whereby the lime, magnesia, and ferric oxide are converted into insoluble carbonates. The mass is dissolved in water, and the solution filtered. As the solution may contain sodium aluminate, it is acidified with hydrochloric acid treated with a large excess of sodium carbonate, and the alumina collected on a tared filter. The insoluble portion of the fused mass, containing the chief portion of the alumina, is fused with a few grms. of pure soda, and the fused product digested with water and the solution treated for alumina as above described. The precipitates are collected, thoroughly washed, dried, ignited, and weighed. If any considerable proportion of phosphate is present, the phosphoric acid should be estimated and deducted from the total weight, the difference being Al_2O_3.

Adulteration of wine. Of the various processes already described which, strictly speaking, might be considered as 'adulteration,' some, as fortifying with spirit, sweetening with sugar, glucose, or glycerol and 'plastering,' are defended as legitimate trade practices of long standing or are officially tolerated within certain limits. Others, as dilution with water, the addition of antiseptics, astringents, colouring matters, and mineral acids, and of potassium hydrogen tartrate and œnanthic ether to give the fictitious character of age, have, as a rule, no other object than that of fraud.

In addition, wine is mixed with the juice of fruit other than the grape, and spurious wines containing no grape-juice whatever are made to simulate well-known types, as port, sherry, claret, and burgundy. The fruit basis of these is usually apple juice, the other principal ingredients employed being crushed raisins, alcohol, sugar, tartar, flavouring essences, and colouring matters derived generally from the juice of such fruits as bilberry, elderberry, black currant, &c.

For the detection of dilution with water, fortifying with spirit, the addition of acids, tartar, glycerol, sugar, and other forms of sophistication of wines, reliance is placed in France and Germany upon the *ratios* which the proportions of the principal constituents of the genuine wines of those countries bear to each other (*e.g.* in France, alcohol : extract (reduced); and in Germany, alcohol : glycerol); and certain maxima and minima are adopted for the constants of genuine wines; but it does not necessarily follow that these can be accepted as standards applicable to the wines made in other countries and by different methods of manufacture. Whenever possible the suspected wine should be compared with a similar wine from the same district and vintage and known to be genuine. A concise and clear *resumé* of these constants and ratios will be found in Allen's Commercial Organic Analysis, 1909, vol. i. 182–186; *see* also Thudichum and Dupré's Treatise on the Origin, Nature, and Varieties of Wine; Windisch's Die chemische Untersuchung und Beurtheilung des Weines; Villiers et Collin, Traité des alterations et falsifications des substances alimentaires; Leach's Food Inspection and Analysis; and Post and Neumann's Traité complet d'analyse chimique appliquée aux essais industriels. J. C.

WINE GUM *v.* GUMS.

WINTER GREEN, OIL OF, *v.* OILS, ESSENTIAL, and SALICYLIC ACID.

WITHERITE. Native barium carbonate ($BaCO_3$) crystallising in the orthorhombic system and isomorphous with aragonite and cerussite. The crystals are, however, invariably twinned, giving rise to pseudo-hexagonal forms; these may be either lenticular or pyramidal in habit, and in the latter case the six-sided pyramids present a certain degree of resemblance to crystals of quartz. Globular aggregates and compact fibrous masses also occur. The colour is white or grey; sp.gr. 4·3; H. 3½. The mineral occurs in some abundance in the lead-bearing veins traversing limestones, &c., at several places in the north of England and on the borders of Shropshire and Montgomeryshire. It has been formed, in some instances at least, by the action of carbonated waters on barytes (L. J. Spencer, Min. Mag. 1910, 15, 310); and it is itself sometimes altered to barytes, as shown by the pseudomorphs of barytes after witherite. The best known locality, which has yielded many finely crystallised specimens, is the Fallowfield mine near Hexham; whilst the largest quantity (about 8000 tons per annum) is produced by the Settlingstones mine also in Northumberland. The mineral is also known from a few foreign localities, but only in small amounts.

Witherite is used in the manufacture of plate glass and porcelain, and for the preparation of barium dioxide (used in the manufacture of hydrogen peroxide), barium hydroxide (for refining beet-sugar), and barium salts (used, *e.g.*, for giving the green light of fireworks). The addition of a small proportion of witherite to clay (1 oz. per cwt.) in brick making prevents any efflorescence and discoloration due to soluble sulphates. Although insoluble in water, it is poisonous, since it is readily acted upon by the gastric juice; and the powdered mineral, mixed with meal, is used as rat poison. L. J. S.

WOAD (*Vouède, Pastel*, Fr.; *Waid*, Ger.).

This commercial product is a dark clay-like preparation made from the leaves of the woad-plant, *Isatis tinctoria* (Linn.), an erect, herbaceous, biennial plant, belonging to the *Cruciferæ*, bearing yellow flowers, small flat elliptical pods, and large smooth lanceolate or spathulate leaves.

The term 'woad' is derived from the Saxon 'wad,' which it has been suggested is derived from Woden, the Saxon God of War. It is synonymous with the Gallic *glastum*, with which, according to Pliny, the ancient Britons dyed their skin blue, in time of war and in connection with certain religious observances.

The plant is a native of Southern Europe, and from very early times has been employed in dyeing blue, for which purpose, previous to the introduction of indigo from India, it was largely cultivated in various parts of Europe—*e.g.* Thuringia, Languedoc, Piedmont, &c. Its cultivation has now declined almost to the vanishing point.

In this country, woad is now only grown, to a very small extent, in the fen lands of Lincolnshire and Huntingdon. The seed is sown in the early spring, March or April, and, the young plants having been duly thinned and weeded, the leaves are ready for the first plucking in June, which, at intervals of 5 or 6 weeks, is repeated once or twice, or as often as fresh leaves shoot up.

The newly-gathered leaves are at once crushed or ground in edge-runner mills to a pulp, which is then placed in small heaps to drain, till sufficiently dry to cohere and be submitted to the 'balling' process. This consists in working the pasty mass by hand into balls, 4–6 ins. in diameter. These are at once spread out on wicker-work trays or 'fleaks,' and thoroughly dried in well-ventilated sheds. The balls are stored in a dry airy place till the whole crop has been gathered, and are then submitted to the so-called 'couching'—*i.e.* a fermentation—process. For this purpose the balls are ground to a coarse powder, which is spread on the floor of the couching-house to a depth of 2 or 3 ft., and there reduced again to the consistency of a paste by frequent sprinkling with water and turning over with shovels. During this process, which lasts from 20 to 40 days, the mass becomes heated and abundant offensive odours are given off. The operation needs to be conducted with some care and skill, so that the fermentation is neither so slow that a 'heavy' product is obtained, nor so rapid as to give one which is 'foxy.' When the fermentation has subsided, and the stiff, pasty mass is sufficiently cooled, it is packed in casks ready for the market.

It has been calculated that 9 parts by weight of woad leaves yield 1 part of the prepared product.

Although woad was formerly used for the indigo contained in it, it is at present only employed for the purpose of exciting fermentation in the indigo-vat ordinarily used by the woollen dyer, which is therefore termed the 'woad-vat.'

According to Wendelstadt and Binz (Ber. 1906, 39, 1627) woad contains two distinct micro-organisms, one of which under suitable conditions appears to be able to reduce indigo.

Spurious woad was sometimes prepared from the leaves of the rhubarb, cabbage, &c., but these products were very inferior to the true woad.

The colouring principle of woad leaves, considered by Schunck to be identical with that present in the *Indigoferæ*, is now known to be a distinct substance. This has not been isolated in a pure condition, but in its general reactions resembles indoxylic acid (*see* Indigo, natural).

Literature.—Chevreul, J. Pharm. Chim. 1808, 66, 369; 1817, 350; Ann. Chim. Phys. 68, 284; Gilbert, Annalen, 41, 245; 42, 315; Trommsdorff, J. Pharm. Chim. 19, 93; Paris, Mus. Hist. Nat. Ann. 18, 251. A. G. P.

WOLFRAMITE or **WOLFRAM.** A mineral consisting of iron and manganese tungstate (Fe,Mn)WO$_4$, crystallising in the monoclinic system. The name *ferberite* is applied to the members at the iron end of the series (FeWO$_4$), and *hübnerite* to those richest in manganese (MnWO$_4$). With this wide difference in composition the percentage of tungsten varies only slightly (WO$_3$, 76·3–76·6 p.c.; analyses of the pure mineral show 74–77 p.c.). The mineral fuses readily before the blowpipe to a black, magnetic bead; and it is decomposed by *aqua regia*, with the separation of yellow tungstic oxide. Distinctly formed crystals are rare, but cleavage masses are of common occurrence. There is a perfect cleavage in one direction, parallel to the plane of symmetry. The mineral is opaque with a bright, sub-metallic lustre and a dark brown to black colour; the streak is dark reddish-brown to black; H. 5½. The high sp.gr. (7·2–7·5) and the perfect cleavage are characters which assist in the identification of the mineral.

Wolframite usually occurs in veins traversing granitic rocks, and is often associated with tin ore. It is, in fact, obtained commercially mainly from tin mining districts; and formerly, before the mineral was of value, it was a source of trouble to the tin miner, since having about the same density as cassiterite it could not be separated from the ore by the ordinary mechanical methods. At one time it was eliminated in a soluble form by fusing the ore with soda (Oxland's process); but now it is extracted by the electromagnet (wolframite being weakly magnetic), and it forms a product as valuable as the tin ore itself. The principal wolfram-producing countries, arranged approximately in the order of their outputs, are: North Queensland (at Wolfram Camp, &c.), United States (Black Hills in South Dakota, Boulder and Gilpin counties in Colorado, Arizona, Nevada, &c.), Portugal, Bolivia, Spain, Cornwall (near Redruth), France, and Rhodesia.

The mineral is used mainly for the manufacture of ferro-tungsten and the hard and tough tungsten-steel, and of some other alloys (*e.g.* 'partinum,' an alloy of tungsten and aluminium). Metallic tungsten is now used as the filament of the so-called 'osram' electric lamps. Wolframite is also used for the preparation of sodium tungstate and other salts.

For bibliography *v.* R. D. George, 1st Rep. Colorado Geol. Survey (1908), 1909; G. P. Merrill, The Non-Metallic Minerals, 2nd ed. New York, 1910; Mennicke, Die Metallurgie des Wolfram's, Berlin, 1911. L. J. S.

WOLLASTONITE *v.* CALCIUM.

WONGSKY, WONGSHY, WONGSCHY, HOANG-TCHY. A Chinese yellow dyestuff. It consists of the fruit of the *Gardenia grandiflora.* According to Rochleder (J. 1858, 475), it contains *rubichloric acid* (*see* MADDER) and *crocin,* the glucoside of *Crocetin,* which is also present in saffron (*Crocus sativus* [Linn.]). Wongsky dyes aluminium and tin mordanted fabrics a yellow, whereas with iron mordant an olive colour is produced.

WOOD APPLE GUM *v.* GUMS.

WOODBURYTYPE *v.* PHOTOGRAPHY.

WOOD, DESTRUCTIVE DISTILLATION OF.[1] Wood completely freed from water has the following composition:—

Carbon, 50 p.c.
Hydrogen, 6 p.c.
Oxygen, 42·75 p.c.
Ash, 1·25 p.c.

The chemical nature of wood may be said to consist principally of cellulose, lignin, water, and of ash-forming materials.

If wood is heated in a closed vessel with the air partly or entirely excluded and the vapours and gases are allowed to escape, the cellulose and lignin molecules are broken up by processes, the nature of which is little understood, but which are characterised by the formation of charcoal, which is left as a residue, and by the formation of gases and vapours, the latter of which, when condensed, is known as pyroligneous acid. P. Klason, Heidenstam and Norlin[2] concluded that the destructive distillation of wood may be represented by the following equation:—

$$\underbrace{2C_{42}H_{60}O_{28}}_{\text{Wood}}=\underbrace{3C_{16}H_{10}O_{2}}_{\text{Charcoal}}+28H_2O+5CO_2+3CO+\underbrace{C_{28}H_{32}O_9}_{\substack{\text{Total amount of products, contained in the pyro-}\\\text{ligneous acid, in the tar, and in the wood gases}}}$$

They proved further that the destructive distillation of cellulose forms the most important products, viz. charcoal, acetic acid and tar; whilst lignin forms principally charcoal, acetic acid, wood alcohol and tar.

The destructive distillation of wood is occasionally carried out for the purpose of producing charcoal only, but at present it is more frequently the case that the by-products, acetic acid and the wood alcohol, are the most important substances yielded.

As regards the value of various kinds of wood for the process of destructive distillation, it has been shown that hard woods give the best yields of charcoal, acetic acid, and wood alcohol, whilst soft woods give smaller amounts of these products. Soft woods, however, show a larger yield than pine wood, which yields, besides the above-named products, a certain amount of turpentine, pine oils and pine tar oils. Local market conditions must decide in each case what is the most desirable wood for the purpose.

All wood for destructive distillation is split into cord-wood averaging 6 ins. in diameter and 4 ft. long. This initial preparation is usually carried out in the forest, but at manufactories recently erected in the United States large logs are brought to the saw mill where all the timber is utilised, and only those logs unfit for other purposes are used for cord wood. The cord wood is stacked in an exposed situation if possible, where it is allowed to dry and season for about 18 months, after which the moisture content will be found to be quite constant. The length of time required for this seasoning varies with the climate, and although it is thought that the moisture content of 20 p.c. is the most desirable, it is frequently found necessary to use wood containing 30 p.c. or more. A high percentage of moisture in the wood is undesirable owing to the fact that it delays the distilling process, decreases the yields of acetic acid, wood alcohol and charcoal, whilst at the same time it increases the amount of noncondensable gases and also the amount of fuel used for the purpose of supplying heat for the distillation.

The process of destructive distillation is carried out in closed vessels built of brick or iron, and heated either by allowing the products of combustion to come directly in contact with the wood, excluding any excess of air; or by transmitting the heat through the walls of the vessel. In either case the distilling apparatus is connected with a condenser, the purpose of which is to condense the vapours formed during the reaction.

The apparatus for the destructive distillation of wood may be said to consist of three principal parts:—

1st. The container for the wood.

2nd. The arrangement for generating and supplying the heat to the container.

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[1] M. Klar, Technologie der Holzverkohlung, 1910. Second Edition. Julius Springer, Berlin.

[2] Ark. Kemi Min. u. Geol., 1908, Bd. 3, 9.

3rd. A condenser connected with the container by an intermediate vapour pipe.

After the wood has been placed in the distilling apparatus and the heating started, the water contained in the wood is first driven off; when this is accomplished the destructive distillation of the cellulose and lignin begins and will be indicated by the formation of non-condensable gases and by the appearance of the so-called pyroligneous acid, a brown liquor of characteristic odour, in which considerable tar is found. When the temperature reaches 270° an exothermic reaction sets in which supplies most of the heat necessary for the distillation process. The end of the process will be indicated by the cooling of the pipe which connects the distilling apparatus with the condenser.

In carrying out this distilling process on a commercial scale, the three phases of the distillation, namely: the expulsion of the water, the heating of the wood to the point at which the exothermic reaction sets in, and the completion of the process by means of the above-named reaction, will not necessarily take place consecutively, owing to the fact that the large-sized apparatus used will not allow the heat to be transmitted uniformly to all the wood in the vessel. Hence part of the wood situated near the heating surface may be in the third phase of the process, whilst that not so near the source of heat may be still in the first phase.

In general, yields of various products from air-dried hard wood in percentage by weight will be as follows:—

Charcoal, 25 to 27 p.c.
Crude pyroligneous acid, 45 to 50 p.c.
Gases, 25 to 28 p.c.

The composition of the charcoal will be variable, depending upon the process used and particularly upon the temperature at which the distillation has been finished. The following table gives the composition of charcoal produced by several processes:—

Process	P.c. C	P.c. H	P.c. O+N	P.c. ash	Temperature
Old 'Meiler' process	90·36	2·74	5·72	1·1	above 600°
Kiln process	84·18	3·32	11·72	0·78	450°
Retort process	81·15	4·24	13·64	0·97	350°

The *crude pyroligneous acid* will be found to be composed chiefly as follows:—

Water, 81 p.c.
Wood alcohol, 3 to 4 p.c.
Acetic acid, 6 to 8 p.c.
Dissolved and suspended tar, 7 p.c.

Other compounds contained, such as aldehydes, ketones, allyl alcohol, amines, phenols, and hydrocarbons are not of commercial importance and are of interest only in the refining of wood alcohol. The wood tar obtained from hard wood has little commercial value and is generally used as fuel. Small amounts, however, are used for the manufacture of creosote and wood tar pitch.

The *non-condensable gas* obtained by the destructive distillation of wood, amounting to 25–28 p.c. of the weight of the wood, varies in composition during the different phases of the process, and is composed on an average of carbon dioxide, 60 p.c.; carbon monoxide, 30 p.c.; hydrogen and hydrocarbons, 10 p.c. This gas is generally used for heating the retorts or boilers, and its heating value is equivalent to about 4–5 p.c. of the heating value of the wood decomposed in the process of distillation.

Destructive Distillation of Pine Wood.

The destructive distillation of pine wood containing rosin and turpentine, besides the cellulose and lignin, will produce products different from those obtained from hard wood. The turpentine being volatile with water vapour is almost completely distilled over during the first phase of the distillation. In this phase, also, the rosin melting and flowing from the wood cells, covers the surface of the wood and the bottom of the distillation retort. During the second phase, this rosin will be decomposed, yielding such products as pinoline, rosin oils, and a residue of rosin coke. The pinoline will be mixed, more or less, with the turpentine originally contained in the wood, the rosin oils will combine with the tar formed in the usual course of wood distillation, and the rosin coke will be mixed with the charcoal. The mixture of turpentine and pinoline is known as crude wood turpentine. The presence of the rosin oils in the pine wood tar gives it a peculiar orange colour when painted on wood, which property makes it of considerable value. The amounts of acetic acid, wood alcohol and charcoal obtained from pine wood are considerably less than in the case of hard wood distillation.

An active demand for wood turpentine, for pine wood tar and pine wood tar oils, with good prices for these products and cheap prices for the wood, may cause, under certain circumstances, pine wood to be preferred to hard wood. But these conditions will not be frequent, and since the yields of acetic acid and wood alcohol and also of charcoal are considerably less, as the container can be filled with a larger weight of hard wood than of pine wood (on account of the lower specific gravity of the latter), the efficiency of a distilling plant using hard wood is higher than one of the same size employing pine wood.

Various Forms of Distilling Apparatus for Cord Wood.

The number of forms of apparatus actually used for this purpose is large, and still larger is the number of designs which have been described in the literature or by patents taken out in different countries.

Only the most important types in practical use are given in what follows.

I. Distilling Apparatus made of Brick.

a. *Charring of the wood in brick kilns by fire gases which come directly in contact with the wood.*

1. *Fire gases generated inside the distilling apparatus by burning a part of the charge.* To this type belongs the so-called 'American kiln,' seen in Fig. 1. This apparatus consists of a brick chamber, of about 15,000 cubic ft. capacity, holding 80 cords of wood filled in by a top iron door *a*. There is a bottom iron door provided for discharging the charcoal. 4 ins. × 4 ins. air inlet holes *d*, *d* are provided in the lower parts of

the wall, and a couple of these kilns are connected by a brick goose neck *e* with the main smoke pipe, mostly built of wood. This main smoke pipe connects the kilns with the condenser plant *f g h*, and a fan is used for transporting the vapours and the gases from the kilns to the condensers and also for supplying the kilns with a certain amount of air, sufficient to generate the heat required for the destructive distillation of the wood by burning a certain amount of the wood, but avoiding any excess of air.

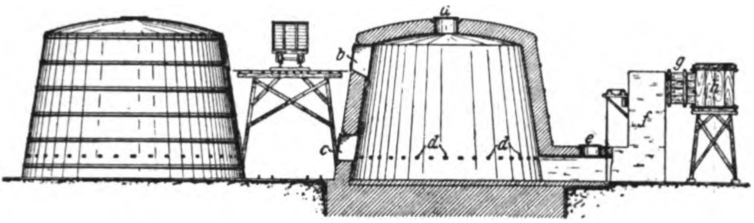


Fig. 1.

Brick wood-distilling apparatus for an 80-cord charge heated by burning a portion of the charge.

In the large plants at work in Michigan, often as many as 80 kilns are connected with condensers, using as much as 250 cords of wood per day, and condensing up to 50,000 gallons of crude pryoligneous acid. Unfortunately these kilns do not afford the proper amount of volatile by-products (acetic acid and wood alcohol) and about 50 p.c. of the possible yield is lost by being burnt to carbon dioxide and water. These kilns should only be used when wood is very cheap and fuel and labour prices high and when there is not much demand for calcium acetate and wood alcohol. As these conditions seldom coexist, the kiln system must be considered wasteful and should be no longer used.

2. *Fire gases are generated outside of the distilling apparatus by fuel (mostly wood) in a special fireplace and conducted from there to the wood.* Fig. 2 represents such a type, originally known as the 'Schwartz kiln.' The Swedish kilns of Ljungberg and of Ottelinska are of a similar type.

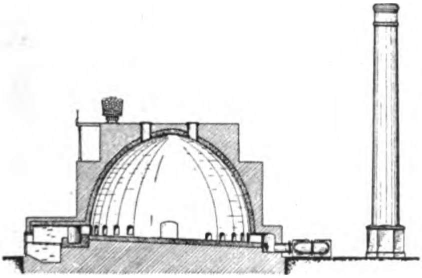


Fig. 2.

Brick wood-distilling apparatus, according to Schwartz, heated by a special open fire.

b. *Heating the wood in brick kilns by fire gas which, passed through radiators, transmits the heat by radiation to the wood.*

Inside a brick chamber, cast-iron or steel radiators are provided, through which fire gases are passed, which transmit the heat by radiation to the wood surrounding these radiators.

The oldest type of this kind of a wood distilling apparatus is represented by the 'Reichenback kiln.'

Sweden developed a new form of this type called the 'Tube Oven,' seen in Fig. 3.

These brick kilns do not permit the charcoal to be discharged immediately after the distillation is finished. In fact, every hole of the oven has to be closed by bricks so as to allow the charcoal to cool with absolute exclusion of air. This cooling process requires, in the case of large sized kilns (50 cords or more) as much as eight days, and the efficiency is decreased correspondingly. In order to discharge the charcoal from kilns heated by radiators, immediately after the close of the distillation, the wood must be loaded on iron cars capable of being pulled or pushed into the brick container. After the distillation is finished the cars, loaded with hot charcoal, are pulled out quickly and transferred to a steel chamber of the shape of the brick container, when cooling will not require more than 24 to 48 hours. After the cars are withdrawn, other cars, already loaded with new wood and ready for charging, will be put into the brick chamber, still hot by the previous operation.

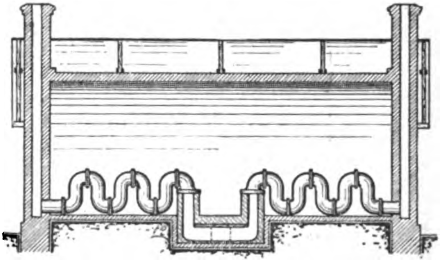


Fig. 3.

Brick wood-distilling apparatus heated by steel coil radiators.

These brick kilns, heated by radiators, charged and discharged by iron cars, are the newest form of brick distilling apparatus.

A distilling apparatus built of brick is cheaper to build and possibly cheaper to maintain, but gives lower yields than steel apparatus as regards acetic acid and wood alcohol, on account of the difficulty of preventing the brick walls from leaking.

II. Steel Distilling Apparatus.

A. *Intermittently operated apparatus.*

The most important representative of this type is the Swedish 'Carboven,' shown in Fig. 4. This apparatus can be loaded with 100 cords of wood, and will require about three weeks for filling, distilling, cooling and discharging.

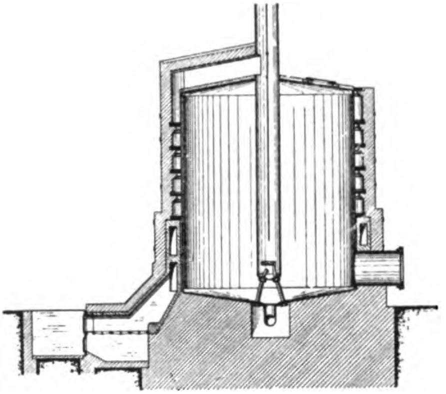


FIG. 4.

Vertical steel wood-distilling apparatus for large charges, heated by fire-gases circulating around the steel container, called 'Carboven'; used in Sweden.

A couple of inner vertical heating tubes, instead of one large one, is the characteristic feature of the bosnic steel distilling apparatus.

B. *Apparatus for discharging the charcoal immediately after the close of the distillation without cooling the charcoal before discharging.*

1. *Horizontal types.*—*a. Apparatus for small charges.* To these belong the distilling apparatus, generally called 'retorts,' largely used in the past and still employed in Germany, Austria, Russia, Pennsylvania, and other countries or states. These retorts are about 39 ins. in diameter by 10 ft. in length, are round in section, and contain ½ cord wood. But they are also built for one cord capacity. Usually, one pair of these retorts is heated by the same fireplace, the products of combustion being conducted around the horizontally placed steel cylinders. One side of the retort is provided with a cast-iron door, the other tight end with a nozzle which serves to connect the retort with a condenser (see Fig. 5).

The wood is loaded by hand into these retorts. Inside the retort there is a semicircular scraper, which is pushed to the rear before the retort is loaded and is provided with a rod with a handle ending near the door. After the distillation is finished, a steel container is placed underneath the front of the door. The door is opened, and by means of the scraper the hot and burning charcoal is quickly emptied into the steel container, the cover of which is then closed air tight. A new charge is loaded immediately after discharging. While the new charge is distilling, the charcoal cools inside the container, which is built of thin sheet steel.

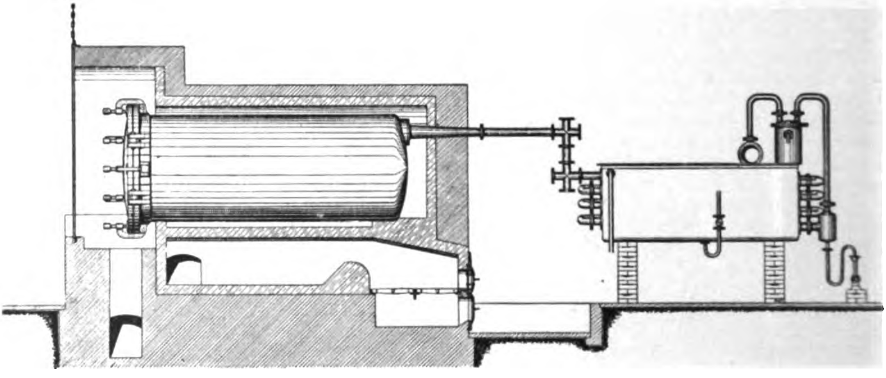


FIG. 5.

Horizontal steel retort for small charges; type, F. H. Meyer, Hanover-Hainholz.

As one of these 39 ins. × 10 ft. retorts can handle only ¾ cord of wood in 24 hours, this type of distilling apparatus is not well adapted for the destructive distillation of wood on a large scale.

These small, horizontal retorts have the further disadvantage that the scraper used in discharging them causes much of the charcoal to be broken into small pieces. The charging of the retort by hand also requires many workmen, causing loss of time and decreasing the efficiency of the plant.

β. Wood-distilling apparatus for large charges arranged for mechanically charging and discharging. The disadvantages above mentioned may be avoided by employing retorts of large capacity, provided with mechanical contrivances for filling them with wood and also for discharging the charcoal. The distilling apparatus which meets these conditions best is the so-called 'car retort.' A distilling apparatus of this kind consists of a horizontal steel retort, capable of working off a charge of 6 to 10 cords of wood (see Fig. 6). The wood is loaded on cars which are pulled or pushed into the retort; this has rails on the bottom and, according to its capacity, one or two doors for filling and discharging. Each car, made of steel, contains

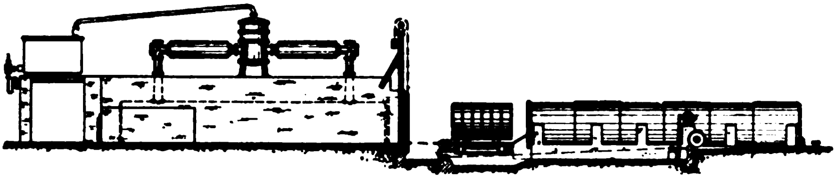


FIG. 6.

Horizontal steel retort, filled and discharged by cars; for charges up to 10 cords; type, F. H. Meyer, Hanover-Hainholz.

usually two cords of wood. The retort is connected by necks with one or two condensers of the usual tube type. The heating of these retorts is mainly effected by an open wood or coal fire and, to some extent, also by burning the tar and the gases obtained in the destructive distillation of the wood. The combustion gases travel by flues round the retort and escape in a smoke stack. The heating by an open fire has latterly been replaced by producer-gas, obtained either in the usual way, that is generated by gas producers, or as a by-product in the destructive distillation of the wood. A gas-heated retort will last longer, will use less fuel and will yield higher results. The question of the best kind of gas producer for this purpose is dealt with later. After the distillation is finished the doors of the retort are opened and the cars, containing the hot charcoal, withdrawn and transferred as soon as possible to a horizontal steel cylinder, exactly corresponding in shape with the retort and also provided with doors for filling and discharging. The withdrawal of the cars is mostly done by means of a locomotive or by means of transportable electric or steam hoists, and has to be done quickly in order to avoid the combustion of the charcoal. After the cars containing the hot charcoal are transferred to the horizontal steel cylinder, placed opposite the retort, the doors of the cylinder are closed air tight and the charcoal allowed to cool with exclusion of air. The cooling requires, according to the weather and character of the wood, from 24 to 40 hours.

This kind of wood-distilling apparatus further allows of the preliminary heating of the wood before filling it into the retort, by means of the waste combustion gases, which escape from the last retort flue into the smoke stack. In order to utilise this waste heat, the cars loaded with the wood are placed in a brick channel located opposite the charging door of the retort. The waste combustion gases are driven over the wood by means of a fan.

Fig. 6 shows a modern distilling apparatus, having a higher efficiency than any other wood-distilling apparatus in practical operation.

A charge of 10 cords of wood is worked off in 24 hours, including filling, distilling and discharging, and it requires also very few workmen to attend to the firing, charging and discharging. By discharging the charcoal in a cold state and without the use of scrapers, a better class charcoal is obtained with the production of only a very small amount of powder or small pieces.

A revolving retort of a capacity corresponding to a charge of 6 to 10 cords of wood has been tried but discarded on account of the difficulty of contriving proper outlets and of keeping these outlets tight. Moreover, revolving retorts gave, of course, large amounts of charcoal powder and small charcoal.

2. *Vertical steel retorts.* Vertical steel retorts, either built stationary or transportable, are in use in Germany, Belgium, France, Italy, and also in Russia. France, in particular, is the country of vertical retorts, which are almost always constructed as transportable ones. These retorts contain a charge of 1 to 1½ cords of wood and are heated by an open fire or by a gas fire from underneath (see Fig. 7). They are filled outside of the settings, after being placed in a horizontal position. After the retort is loaded and closed it is lifted, by means of a travelling crane, above the open space in the settings to which the retort belongs. Then the retort is lowered into its place and its cover connected by means of a copper goose-neck, with the condenser. After the distillation is finished, this copper goose-neck is taken off, the goose-neck hole in the cover closed, and then the whole retort is lifted out of the settings by means of the crane and transported outside of the building, placed in a horizontal position and then allowed to cool down, which will require from 12 to 24 hours, according to the charge and the

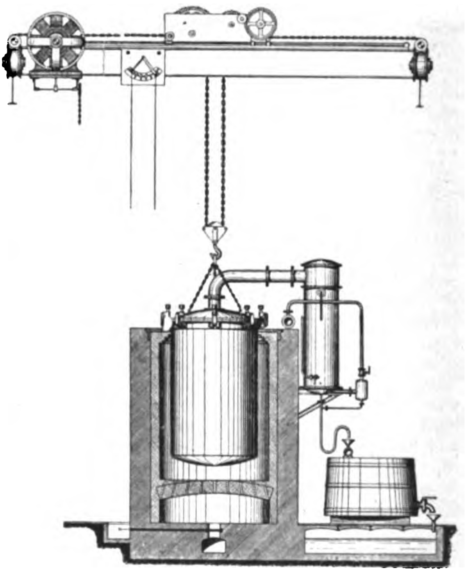


FIG. 7.

Vertical transportable retort; type, F. H. Meyer, Hanover-Hainholz.

weather. These retorts give good yields and afford good charcoal, but their efficiency is not so good as that of the car retorts already described.

Sometimes these vertical retorts are constructed stationary and provided with a charcoal discharging door on the bottom. They are not as convenient as the transportable ones and do not give the same quality of charcoal, because the discharging is done by dumping, which cause breakages of the charcoal.

C. *Continuously-working wood-distilling apparatus.*

The distilling apparatus above described is either operated intermittently or only partly continuously.

But there are some types of distilling apparatus which are designed for continuous working, as, for instance, the Swedish Groendal retort, which belongs to the type of the car retorts described on p. 777.

The Groendal retort consists of three main parts, namely:

1st. The drying chamber, built either of brick or of steel.

2nd. The distilling apparatus consisting of a horizontal steel retort.

3rd. The cooling apparatus for the charcoal, consisting of a steel cylinder of the shape of the retort.

These three parts are connected together but can be separated one from the other by means of vertical sliding doors of iron. The wood, loaded on cars, is filled in the drying chamber through which the exhaust combustion gases, escaping from the retort flues, are passed. After the drying is complete, the sliding doors between this drying chamber and the retort are lifted and the load transferred into the distilling zone of the system. This distilling apparatus is heated by any kind of heat generated by open fire or gas producers. The combustion gases travel around the steel shells, thus transmitting the heat to the wood inside the shell.

After the wood cars have passed the distilling part of the system, another slide door is opened and the cars with the finished charcoal are transferred into the charcoal cooling chamber, through which the cold non-condensable gases, escaping from the condensers of the wood-distilling apparatus, are passed in order to do the cooling work and preheat the gases. A double sliding door at the other end of the system allows the cooled cars with the cooled charcoal to be continuously passed out.

Another continuously working wood-distilling apparatus which may be mentioned here is the wood-gas producer, which, however, does not yield any charcoal. This wood-gas producer is used for the generating of heating gas from second-class cord wood or wood refuse in order to heat boilers and retorts, but also to recover, at the same time, the by-products of the destructive distillation of wood, viz. acetic acid and wood alcohol. These gas producers (Fig. 8) consist of a vertical brick or brick-lined steel furnace provided on the top with a funnel with double doors for filling the gas producer with wood while in work. The bottom of this gas producer is provided with an iron grate through which a certain amount of air is allowed to enter. The upper part is connected with a condenser. In order to start the gas producers, charcoal has to be put upon the grate and allowed to become red hot. Then the filling in of the wood is started by means of the double-door funnel above-mentioned. The condenser, connected with this gas producer, communicates by means of a gas flue with the smoke stack of the boilers or the retorts, and by the natural draught of this smoke stack a certain amount of air enters through the grate into the gas producer, generating producer gas when coming in contact with the hot charcoal. This hot producer gas carbonises the wood on the top of the charcoal zone on its way up to the outlet, and forms, at the same time, the products of the destructive distillation. These escape, together with the producer gas obtained by passing air through the hot charcoal layer, into the condenser, and while the non-condensable gases escape by the main gas flue, the vapours of pyroligneous acid and of tar are condensed and discharged by means of a siphon. In such a gas producer, there will be a hot charcoal zone on the bottom, above this there will be wood in the distilling state, and above this zone there will be another zone of wood in the drying period, and on the top of this drying zone there will be the zone of the green wood, filled through the funnel.

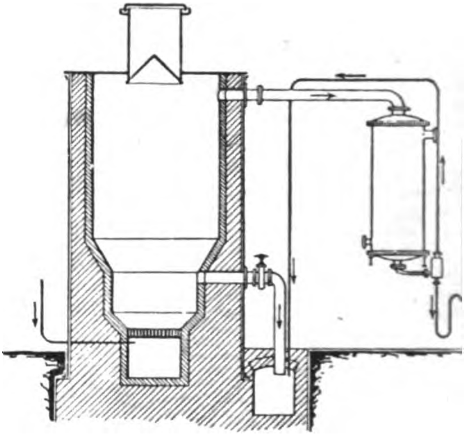


FIG. 8.

Wood-gas producers; type, F. H. Meyer. Hanover-Hainholz.

These gas producers are not very efficient; they yield no charcoal and only 50 p.c. of the amount of acetic acid and wood alcohol obtainable from the same amount of wood when distilled in retorts. But considering that they produce heating gas and at the same time allow 50 p.c. of the acetic acid and the wood alcohol to be recovered, they are important and economical in working under favourable conditions.

Apparatus for the destructive distillation of pine wood, rich in turpentine and rosin. As already mentioned, some varieties of pine wood contain, besides cellulose and lignin, large quantities of rosin and turpentine.

As it is the purpose of the pine wood distillation to separate the turpentine in its original state as much as possible before the destructive distillation of the cellulose, lignin and rosin sets in, the apparatus for the destructive distillation of pine wood of this kind must be provided by a heating system which allows a uniform transmission of heat to any and every part of the wood contained in the retort, or which at least allows the temperature to be under control.

It has been proposed to heat the retorts for this purpose by electricity instead of by an open fire or by superheated air or gases circulating around the retort; by oil or metal bath contained in a double jacket; or by superheated steam brought directly in contact with the wood.

These proposals are still in the experimental stage, but it would seem that these methods of heating are too expensive, inasmuch as a carefully designed gas-heating system, using gas producer gas or natural gas, will do the same work more economically.

Any one of the apparatus already described may in general be employed for pine wood distillation. But for recovering the turpentine in its original state, or at least not very much contaminated with the products of the destructive distillation of the wood and rosin, the smaller units (6 cords capacity) of car retorts, heated by means of uniformly distributed gas burners, are most to be recommended.

DESTRUCTIVE DISTILLATION OF WASTE WOOD OR SPENT WOOD.

The splitting of the logs and cutting these into cord wood furnishes a large amount of small-sized wood waste. Also cutting the log into timber and working up the timber furnishes another class of waste wood known as slabs, edgings, shavings, sawdust, and so on.

As long as this wood waste consists of pieces large enough to furnish charcoal of the usual size, it can be handled just as cord wood in the standard retorts, and it will yield almost the same amount of charcoal, wood alcohol and calcium acetate as cord wood obtained from the same log, when these figures are referred to the weight and not to the volume of the wood, as a cord of slabs or edgings will weigh very much less than a cord of real cord wood.

With regard to the destructive distillation of sawdust or shavings, this raw material is not capable of being distilled in any one of the standard apparatus previously described, on account of its voluminous character or by reason of the fact that there is not enough air space between the small, single wood pieces whereby the escape of the vapours and gases, formed on distillation, is rendered impossible. Back pressure, and under unfavourable circumstances even an explosion, will be the consequence of trying to distil sawdust or other wood of this form in the standard wood-distilling apparatus.

There have been numerous proposals to distil sawdust or other fine wood, and almost every one of these proposals is based either on the use of thin layers of sawdust or the use of stirring contrivances, or of a combined system of thin sawdust layers and stirring contrivances or scrapers, or finally on the briquetting of the sawdust before it is distilled.

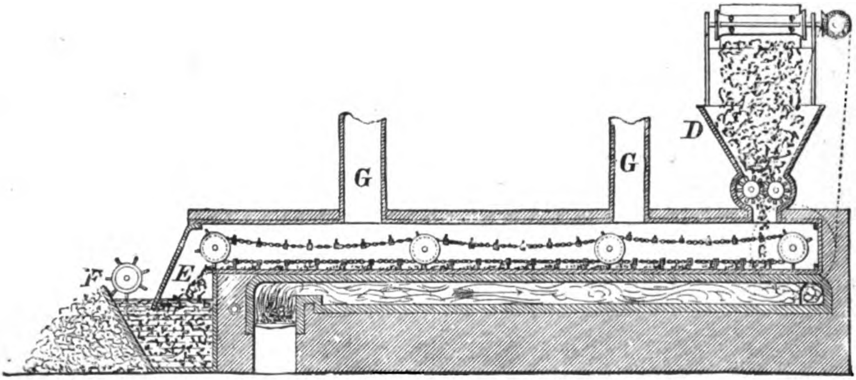


FIG. 9.

Retort for distilling small wood waste.

None of these apparatus has taken a practical form, at least on a large scale. Up to the present time, neither small nor large plants which handle sawdust or a similar class of wood, are operated economically on account of the large initial outlay, which is out of proportion to the value of the output and on account of the fact that there is no market, at a sufficient price, for the large quantities of charcoal powder produced.

Figs. 9 and 10 show types of apparatus which are used for this purpose. The apparatus (Fig. 9) transfers the sawdust continuously by means of scrapers over fire-heated steel plates, while in the apparatus in Fig. 10 the sawdust continuously drops down in thin layers by its own gravity between the space of the fire-heated shell of the vertical retort and the cast-iron rings, which serve as outlets for the vapours and gases.

TREATING THE CRUDE PYROLIGNEOUS ACID.

Crude pyroligneous acid consists of a watery solution containing acetic acid, wood alcohol and its companions (aldehydes, ethers, ketones, allyl alcohol, phenols) and tarry matters in solution. This brown liquid is further mixed with tar in suspension.

Crude pyroligneous acid cannot be sold in large quantities, but acetate of lime and crude wood alcohol are in large demand.

The object of treating the crude pyroligneous acid is to separate the acetic acid and the wood alcohol from the water and the tarry materials.

First the tar, suspended in the liquid, is separated by allowing the liquor to stand. The tar will settle either on the top or on the bottom of the pyroligneous acid and is then drawn off.

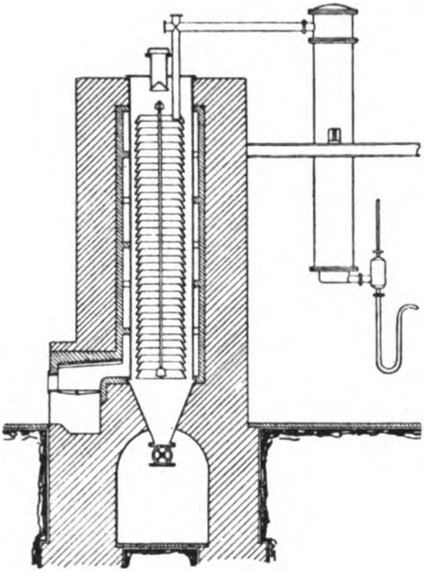


Fig. 10.

Vertical retort for the continuous distillation of small wood waste; type, F. H. Meyer.

But the remaining liquid still holds tar in solution and this dissolved tar must be separated in order to make marketable acetate of lime, which must contain at least 80 to 82 p.c. $(CH_3COO)_2Ca$.

There are several methods employed in order to separate the tarry matters in solution or suspension from the crude pyroligneous acid. The oldest process, still in use in some plants, consists in a simple redistillation of the crude pyroligneous acid in copper stills, connected with a condenser and heated either by an open fire or better by a steam coil (Fig. 11). The tar remains as a residue. The distillate is a more or less water-white liquid, which is now practically free from tar and contains principally water, acetic acid, wood alcohol and its associated products above mentioned.

This method of removing the dissolved tar by simple distillation requires about 50 p.c. of the total amount of fuel or steam generated in a wood-distilling plant.

The author of this article introduced new methods of distillation of the crude pyroligneous acid, and up to date the crude pyroligneous acid of about 1000 cords of wood is so treated.

This process is based on the principle of the multiple effect evaporators, originally used in the manufacture of sugar (Fig. 12). Two or more distilling stills are used, one connected with the other and provided with contrivances to maintain a different but gradually lowered boiling-point or a different but gradually lowered working pressure in each one of the stills. For instance, still 1 will be heated by steam of 15 lbs. pressure, using a steam coil or any other heating contrivance.

The liquor, surrounding this steam-heated contrivance, is kept under atmospheric pressure. The pyroligneous acid vapours, generated in still 1 by means of the heating effect of the steam, enter the heating contrivance of the second still, kept under a lower pressure by means of vacuum and therefore a lower boiling-point of the liquid than in still 1. Therefore the pyroligneous acid vapours, escaping from the first still, heat and distil the crude pyroligneous acid in the second still. This system can be continued indefinitely theoretically, but a system of four combined stills is all that can be reached practically.

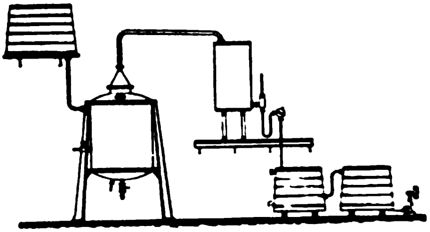


Fig. 11.

Apparatus for distilling crude pyroligneous acid; type, F. H. Meyer.

A distilling apparatus of this type requires only one-third of the amount of steam or fuel hitherto used for distilling the crude pyroligneous acid in simple distilling apparatus; or the saving may amount to 100 p.c. when sufficient exhaust steam is available. Fig. 12 shows such an installation, based on the multiple effect distilling system.

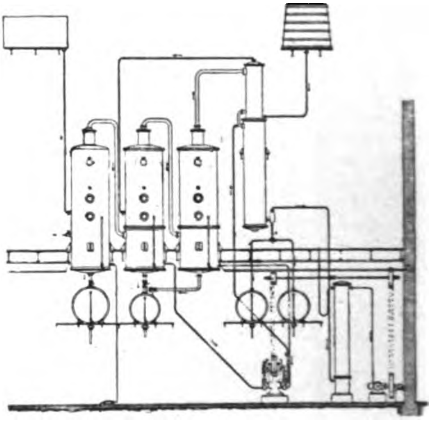


Fig. 12.

Apparatus for continuous distillation of crude pyroligneous acid in multiple effect distillers; type, F. H. Meyer.

Besides these two processes, used for redistilling the crude pyroligneous acid, there is another, employed more particularly in German plants.

This process combines the distillation of the crude pyroligneous acid with the neutralisation of the tar-free distillate by means of milk of lime or soda ash and the separation of the wood alcohol from the acetate solution.

The pyroligneous acid is distilled in a copper still, heated by a steam coil. Instead of passing the vapours of pyroligneous acid into a condenser, they are forced through milk of lime or soda ash solution, contained in closed copper or iron tanks, which are connected with a condenser (Fig. 13). The acetic acid thus combines with the lime or the soda, forming acetate solutions, whilst the wood alcohol and water vapours escape to the condenser from which an aqueous solution of the alcohol is discharged containing 5 to 12 p.c. wood spirit.

All the processes described above for removing tarry matters before treating the pyroligneous acid with milk of lime or soda ash solution, are based on the *distillation principle* and handle the gross distillate discharged from the condensers connected with the wood distilling apparatus.

The writer has introduced another patented process which is not based on the redistillation of crude pyroligneous acid, but depends on separating the total amount of tarry matters from the vapours escaping from the wood-distilling apparatus *before* these vapours are condensed. This is effected by washing the vapours and gases by means of crude wood tar or a mixture of crude wood tar and pyroligneous acid in two or more gas washing apparatus, which are combined together, and maintaining in each one a gradually decreasing temperature.

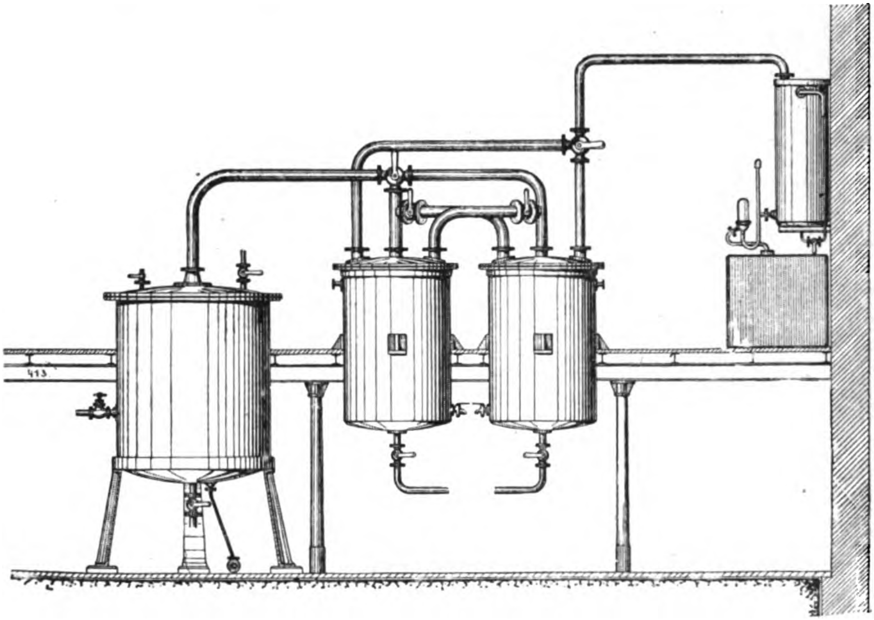


Fig. 13.

Apparatus for distilling crude pyroligneous acid by passing acid vapours through layers of milk of lime; type, F. H. Meyer.

For instance, in the tar washer 1, a temperature of about 300°F. may be maintained and in the last tar washer, or the washer next the condenser, a temperature of 212°F. may be maintained.

By the combined effect of the fractional condensation of the tar and of the absorbing affinity of the large amounts of tar used as a washing liquid, for the small amounts of tar contained in the form of vapours in the products, the pyroligneous acid discharged from the condenser will be practically free from tar and ready to be neutralised by milk of lime or soda ash.

This process is successfully used in many wood-distilling plants and saves entirely the expenses of the redistillation of the crude liquor.

Manufacture of Acetate of Lime from Crude Pyroligneous Acid.

As already mentioned, gray acetate of lime 80 to 82 p.c., is the product into which the acetic acid, contained in the pyroligneous acid, has to be transformed for the purposes of shipment.

The manufacture of gray acetate of lime starts with the tar-free distillate, obtained from the crude tar containing pyroligneous acid by one of the processes already described. This distillate is neutralised either by mixing it with milk of lime in a wooden tank, provided with a stirrer and cover, or by passing the vapours through layers of milk of lime.

The milk of lime combines with the acetic acid; it partly saponifies any methyl acetate; it transforms some of the aldehydes into insoluble rosins; and it combines with phenols, forming insoluble lime compounds. After adding the milk of lime, the neutralised liquor is allowed to stand in order that the precipitates, formed by the neutralising processes, shall settle.

The next operation on the settled liquid, containing principally wood alcohol and its associates, acetate of lime and water, consists in separating the wood alcohol from the aqueous solution of the acetate of lime, either in form of a weak alcohol solution by means of a simple intermittently operated still, or in form of concentrated wood alcohol by means of an intermittently or continuously operated rectifier.

The simple distilling still furnishes a weak wood alcohol solution, containing from 8 to 10 p.c. of wood alcohol, whilst the rectifier turns out by a single operation crude wood alcohol from 30 to 95 p.c., depending upon the design of the rectifier.

The simple still consists of a steel or copper still, provided with a copper heating coil and connected with a condenser.

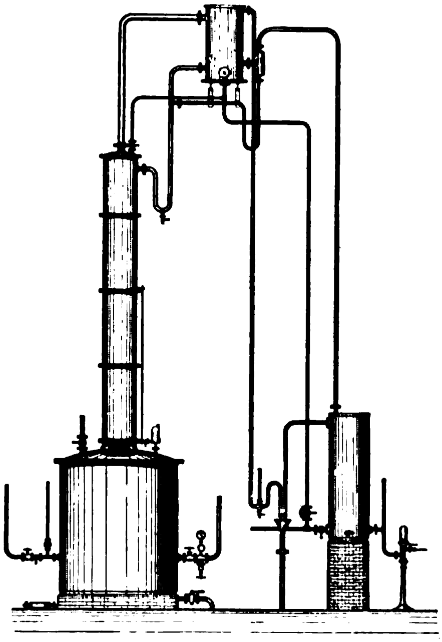


FIG. 14.

Intermittent-working rectifier for wood alcohol; type, F. H. Meyer.

The intermittently operated rectifier, shown in Fig. 14, is built of a steel or copper still with a copper heating coil, a copper column with rectifying sieve or bell plates, a separator and condenser. The working principle of these rectifiers is based on fractional distillation, and the 'columns' used for this purpose are very similar to those employed in manufacturing grain alcohol and known as the 'Savalle apparatus' from the name of the inventor. The continuously working rectifiers, for separating the crude wood alcohol in a concentrated state from the neutralised liquor, are the most modern and most economically working apparatus for this purpose (Fig. 15). They have been introduced in the wood-distilling industry by the author of this article, and they furnish by a single operation the so-called 'crude wood alcohol' of 95 p.c. and separate at the same time the oils, originally contained in the neutralised liquor and also the acetone, if desired.

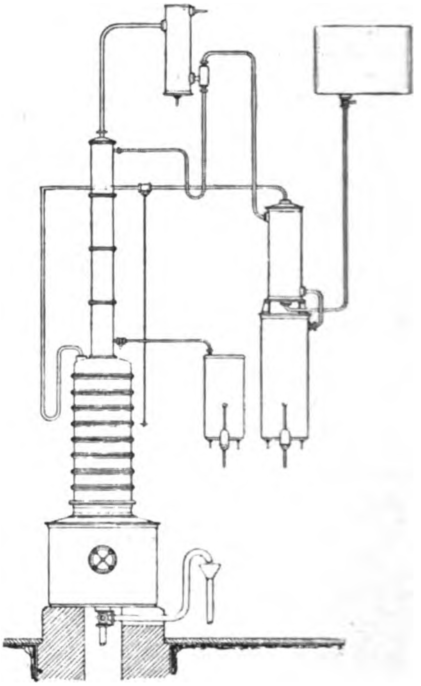


FIG. 15.

Continuous-working rectifier for wood alcohol; type, F. H. Meyer.

The continuously working apparatus are principally built of two columns; at the top of one column the neutralised liquor enters and the second column takes the wood-alcohol vapours escaping from the first column. The neutralised liquor travels in the first column *downwards* from plate to plate and meets on its way down the steam, entering into the bottom section. The wood alcohol, containing about 30 p.c. of wood alcohol and 70 p.c. of water, escapes from the top section of the first column, while the acetate of lime solution freed from wood alcohol, is continuously discharged from the bottom section of this column. The 30 p.c. wood alcohol vapours enter the bottom part of second column, and on their way *upward* from plate to plate they are concentrated by means of fractional distillation and discharged from the top section to a separator and from there to a final condenser, leaving the latter as a product containing up to 95 p.c. wood alcohol.

This product corresponds in chemical composition and physical characters with the so-called 'American Crude Wood Alcohol,' shipped in immense quantities from the United States to Europe. It still contains the total amount of acetone, aldehydes, ketones, esters, ammonia, amines, and allyl alcohol, originally contained in the neutralised liquor, and also some of th 'wood oils,' which always accompany the wood alcohol.

The average composition of this product may be given as follows :—

16 p.c. acetone and other ketones.
6 p.c. aldehydes, methyl acetate, amines, allyl alcohol and oils.
70 p.c. methyl alcohol.
8 p.c. water.

In order to manufacture 'pure' methyl alcohol from the crude wood alcohol, all these contaminating products have to be separated.

This is done by fractional distillation, carried out systematically by means of intermittently or continuously operated rectifiers, similar to those above described. The separation is usually assisted by adding chemicals—for instance, caustic soda and sulphuric acid—which destroy, polymerise, or saponify the products to be separated—for instance, aldehydes, esters, ketones, phenols, amines and so on.

The separation of the acetone and the allyl alcohol, which are always associated with the methyl alcohol, is *entirely done* by a carefully repeated fractional distillation, which yields the concentrated acetone in form of 'head ends' and the allyl alcohol in form of 'tail ends.'

A mixture containing in specified proportion these head ends and tail ends represents the 'denaturing wood alcohol,' used practically everywhere for denaturing alcohol. This material must conform to certain specifications and tests prescribed by the different Governments.

The final product of such a repeated fractional distillation, carried out either by intermittently working or continuously working rectifiers, represents the 'pure' methyl alcohol, which is free from acetone or contains only traces of it, and contains up to 99 p.c. real CH_3OH.

Besides this final product, free from acetone, and the 'denaturing wood alcohol' containing acetone, allyl alcohol, and other impurities, a number of other wood alcohol grades are on the market; for instance, 'pure' methyl alcohol of 99½ p.c. with 0·1 to 1 p.c. of acetone and many other grades demanded by customers.

The pure grades are used for the manufacturing of aniline colours, of formaldehyde, of perfumes; the other grades for varnishes, as solvents, and the poorest grades for denaturing or burning.

The distillation of the neutralised liquor yields, as above shown, two products :

Wood alcohol, as a volatile product;
Acetate of lime solution as a non-volatile residue.

This latter solution holds in suspension insoluble polymerised products, formed by a reaction between phenols and aldehydes with acetate of lime or traces of lime in excess, which must be settled by allowing the liquor to stand.

The settled solution contains varying quantities of acetate of lime, according to the nature of the original liquor and to the process used for distilling off the crude wood alcohol.

These quantities differ from 7 to 25 p.c.; this means, 100 lbs. acetate of lime solution may contain from 7 to 25 lbs. dry acetate of lime, 80–82 p.c. As it is impossible to recover the acetate of lime by a crystallising process on account of its equal solubility in cold and hot water, the solution must be boiled down until the salt is left in the solid state.

Up to the present this boiling was done in two steps. By the first step, the acetate of lime solution is evaporated in open, steam-heated, double-jacket pans (Fig. 16) just to the point at which the concentrated solution becomes solidified by crystallising. This point is reached when the acetate of lime solution contains about 35 to 40 p.c. of the dry salt. The crystallised magma is then spread out in thin layers upon an open drying floor, built of cast-iron plates or steel plates, heated by an open fire or by waste fire gases.

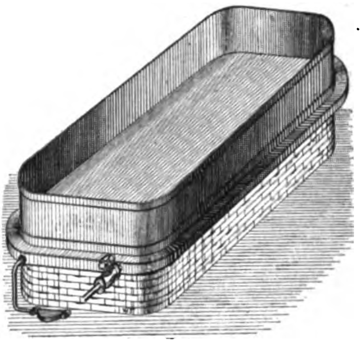


Fig. 16.

Open pan for evaporating acetate of lime solution.

The operation of boiling down the acetate of lime solution to a magma of crystal requires very large amounts of steam on account of the coating of the heating surface by crystals and scales and by the immense reduction of the heat transmitting capacity.

Furthermore, the drying upon an open drying floor necessitates much hand work, as the material must be turned over and gradually transferred from one end of the drying floor to the opposite one, whereby it travels with the current of the fire gases. This ensures that the wet acetate of lime, which can stand a high temperature, comes in contact with the hot fire gases, while the dried salt or partly dried salt comes only in contact with the fire gases of a lower temperature, in order to protect it against decomposition into acetone.

The author has introduced a drying process, in which the solution of acetate of lime will be continuously and mechanically evaporated and dried, doing away entirely with the steam-heated open pans and the high wages required by open drying floors.

By this new process, already in successful operation in plants of all sizes from 30 cords up to 250 cords, the acetate of lime solution is continuously evaporated in specially designed multiple effect evaporating apparatus, operated on the same principle as above described for the multiple green liquor distillers.

The weak solution enters the first evaporator, travels from there to the second, and from the second to the third, leaving the same or the last one as a concentrated liquor, which contains up to 30 to 35 p c. dry salt. This liquor will not crystallise when kept hot.

The liquor flows to a pan into which a rotary drum is dipping, heated inside by steam. This drum becomes coated with a thin layer of the concentrated solution.

While rotating, the thin layer dries quickly, and before the drum dips again into the concentrated solution the magma of crystals, which now coat the surface of the drum, is scraped off by means of knives, working on the surface of the drum (Fig. 17).

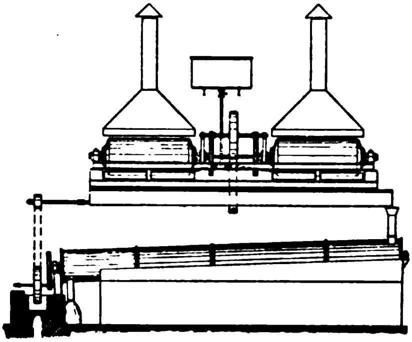


Fig. 17.

Continuous-working rotary evaporator for evaporating and drying acetate of lime; type, F. H. Meyer.

The magma of crystals then travels by means of a conveyor to a belt dryer, built of endless canvas belts or wire cloth belts, upon which the wet salt is transferred against a current of hot air or over pipe coils, heated by exhaust steam. This new type of apparatus for evaporating and drying acetate of lime does away with any kind of hand work; it obviates the disagreeable and unhealthy work of drying upon an open floor; and it saves almost all the wages hitherto spent for drying, and it saves, too, large amounts of fuel. Moreover, the acetate of lime obtained by this process, is of an even form like peas; it does not contain much dust; it is of a brighter colour and is soft and voluminous, yielding on this account more acetic acid and acetone, when worked up into these products.

Manufacture of Acetate of Soda.

Next to acetate of lime, acetate of soda is the most important salt of acetic acid manufactured in wood-distilling factories.

In order to produce sodium acetate in a crystallised state, the distillate of pyroligneous acid, obtained by one of the processes already described, is neutralised by soda ash. The acetate of soda solution is then freed from wood alcohol by the methods before mentioned, and boiled down by open double-jacket pans, or by modern multiple effect evaporating apparatus, until the crystallising point is reached. By the next step the condensed solution is completely dried in cast-iron, fire-heated pans, provided with scrapers, and the heating is continued until the whole of the water is driven off and the anhydrous sodium acetate is completely melted, when the liquid mass will have a temperature of about 320°. At this temperature, sodium acetate is not decomposed, but sodium propionate and butyrate, as well as tarry or resinous matters present in the original product, will be destroyed and converted into insoluble matters.

After melting, the mass is dissolved in water to form a concentrated solution and the charred matter separated by filtering the solution, usually by a filter press. The filtrate is transferred to crystallising vessels and the crystals

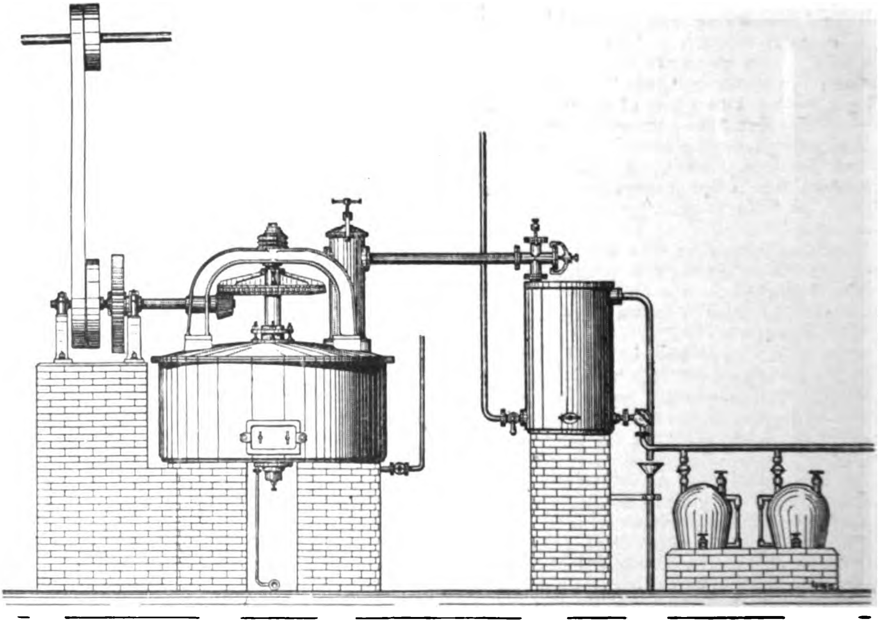


Fig. 18.

Cast-iron still for decomposing acetate of lime by sulphuric acid; type, F. H. Meyer, Hanover-Hainholz.

and mother liquor separated by a centrifugal machine. The crystals are recrystallised and the mother lees returned to the evaporating pans.

Treating of the Primary Marketable Products resulting from the Destructive Distillation of Wood.

The first products resulting from the destructive distillation of wood are: charcoal, crude pyroligneous acid, tar, when hard wood is distilled; or charcoal, crude pyroligneous acid, crude turpentine, crude pine oil and crude pine tar, when pine wood, containing turpentine and rosin, is employed. Of these, the charcoal only is ready for sale. The other products must be further treated in order to convert them into marketable commodities.

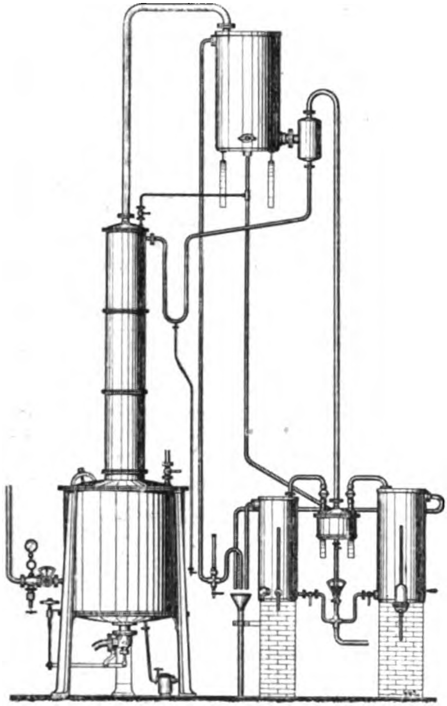


Fig. 19.

Apparatus for rectifying crude acetic acid in order to manufacture glacial acetic acid; type, F. H. Meyer.

From the crude pyroligneous acid acetate of lime, acetate of soda and crude wood alcohol are obtained, and from the latter the 'pure' methyl alcohol, the refined wood alcohol, and the denaturing alcohol as above described.

Many of the wood distilling factories work up the acetate of lime into acetic acid or acetone and the methyl alcohol into formaldehyde.

Manufacture of acetic acid. In order to manufacture acetic acid, only acetate of lime, 80–82 p.c., is used nowadays as raw material. This is mixed with sulphuric acid of 92 to 98 p.c. in a closed cast-iron still, provided with stirrer and scrapers and heated by high-pressure steam, (Fig. 18). After the mixing process is finished the acetic acid is distilled off, a vacuum being maintained in the still during the process of distilling. The crude acetic acid, resulting from the process, contains about 80 p.c. acetic acid (propionic and butyric acid included), traces of sulphur dioxide, and is of a yellow colour. This acid can be used for many purposes in the arts, as, for instance, manufacturing white lead, amyl acetate, &c.

In order to produce 'pure' glacial acetic acid of 96 to 99½ p.c., the crude 80 p.c. acetic acid, obtained by the action of sulphuric acid on acetate of lime, must be rectified in a copper rectifier (Fig. 19).

First a weak acetic acid is obtained containing propionic and butyric acid; then the distillate becomes gradually stronger and after distilling over 40 to 50 p.c. of the original charge, glacial acetic acid distils over: this has a melting-point of 14°–16° and contains 99 to 99½ $CH_3{\cdot}COOH$. At the end of the process the melting-point again falls, and with it the content of acetic acid owing to the presence of propionic and butyric acids.

In order to manufacture 'pure' acetic acid, 99½ p.c., corresponding to the requirements of the pharmacopœas of different countries, the glacial acetic acid, obtained from the first rectification of the crude 80 p.c. acetic acid, will be oxidised and then redistilled by use of a simple still connected with a silver condenser.

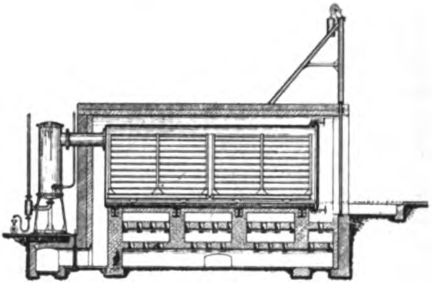


Fig. 20.

Retort for decomposing calcium acetate; type, F. H. Meyer.

Manufacture of acetone. Acetone is manufactured by the dry or destructive distillation of calcium acetate. The process corresponds theoretically with the equation:

$$\left.\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\right\}Ca=CaCO_3+CH_3-CO-CH_3$$

According to the author's patented process, used in most of the existing acetone factories, acetate of lime is spread out in thin layers on steel plates, to be placed one above the other upon platforms on steel cars, allowing sufficient clearance from platform to platform (Fig. 20). These cars are pushed into horizontal steel retorts, heated by fire gases. The retorts are capable of treating from 3000 to 15,000 lbs. of calcium acetate in 24 hours and are connected with a condenser. The destructive distillation sets in at about 300°. After the charge is charred, the cars are withdrawn and other cars, already loaded, charged into the retort.

By the older acetone process, calcium acetate was distilled in charges not exceeding 1000 lbs.

by means of fire-heated, closed, cast-iron pans, provided with a stirrer and scrapers. But these forms of apparatus yielded only 17 lbs. 'pure' acetone from 100 lbs. of calcium acetate instead of from 20 to 21 lbs. as obtained by the process above described.

There is a third process used, based on the distillation of calcium acetate by means of a stream of superheated steam which is brought directly in contact with the acetate.

The crude acetone obtained by one or other processes contains, besides the acetone, tarry matters, formic and acetic acids, aldehydes, ketones formed by the propionic acid and butyric acid originally contained in the crude material, hydrocarbons, and other products.

By means of repeated fractional distillation, assisted by the use of small amounts of caustic soda and sulphuric acid, acetone of 99½ p.c. is obtained, whilst the tarry matters remain in the residue. The acids are fixed by the alkalis, which destroy the aldehydes, and the foreign ketones and hydrocarbons are obtained as 'tail ends' from the rectifier, from the fact that their boiling-point is considerably higher than that of acetone.

FORMALDEHYDE.

This important disinfectant is obtained from the 'pure' methyl alcohol by oxidising it by the oxygen of the air under the influence of catalytic agents: $2CH_3{\cdot}OH+2O=2CH_2O+2H_2O$. The manufacturing process differs in some respects from the theoretical equation, as side reactions set in whereby a part of this formaldehyde is broken up into carbon monoxide and hydrogen, according to the equation $CH_2O=CO+2H$.

The excess of oxygen under the influence of the red hot catalytic material combines with the carbon monoxide as well as the hydrogen:

$$CO+O=CO_2$$
$$H_2+O=H_2O$$

Carbon dioxide and water are products formed by another side reaction.

Theory indicates that 93·75 lbs. of formaldehyde of 100 p.c. should be obtained from 100 lbs. methyl alcohol of 100 p.c., but by the best practical process only 80 lbs. formaldehyde, as a maximum, can be obtained, which means only about 85 p.c. of the theoretical yield.

The product on the market is an aqueous solution of formaldehyde, containing from 35 to 40 p.c. CH_2O by weight. This solution is liable to polymerise, forming paraformaldehyde by the condensation of 3 mols. of CH_2O, a product which is not soluble in water and therefore causes the solution to become more or less turbid.

In order to avoid this polymerisation and to meet commercial demands, various substances are added to the formaldehyde solution. As methyl alcohol has the peculiar property of preventing polymerisation, a certain amount is added to the formaldehyde solution of the market, which averages

35–40 p.c. (by weight)	CH_2O
12–15 p.c.	$CH_3{\cdot}OH$
53–45 p.c.	H_2O

This solution is manufactured by mixing vapours of methyl alcohol with a corresponding amount of air.

The processes adopted for manufacturing formaldehyde differ in regard to the apparatus or contrivances used for furnishing this vapour mixture *of a constant composition*.

About half the factories existing at present are using the author's process, which is a continuous one, whereby liquid methyl alcohol is introduced in the form of a spray into the top section of a so-called 'carburator' (constructed on the same principle as that used for carburetting coal gas with benzene) and at the same time blowing a stream of hot air which enters the bottom of the 'carburator' against the methyl alcohol spray, whereby the methyl alcohol will be evaporated and mixed with the air in the right proportion. The mixture of methyl alcohol vapour and air is passed over the catalytic material, consisting of rolls of copper wire-net heated to about 400°, before allowing the mixture of methyl alcohol and air to enter.

To avoid explosions and to prevent the methyl alcohol burning into carbon dioxide and water, an excess of methyl alcohol must be used.

The product of the reaction, that is the vapours escaping from the apparatus, contain this excess of methyl alcohol, which is recovered by a fractional condensation of the escaping vapours, whereby the formaldehyde solution will be condensed first and the methyl alcohol last.

As already mentioned, the whole process is a continuous one, as methyl alcohol and air enter at one end of the apparatus, and the formaldehyde solution, the excess of the methyl alcohol used, and the nitrogen with the gases formed by the reactions will be discharged, of course each one separately, on the other end of the apparatus (*v.* FORMALDEHYDE).

CRUDE HARD-WOOD TAR.

The hard-wood distilling process yields two kinds of tar, namely: *the settled tar*, deposited from the crude pyroligneous acid; the *residue tar*, obtained as a residue by distilling the crude pyroligneous acid.

The composition of these two varieties of tar is quite different, as the 'residue tar' contains principally pitch and pyroligneous acid, whilst the 'settled tar' contains, besides pitch and pyroligneous acid, the total amount of phenols and hydrocarbons, usually called 'tar oils.'

There are no two samples, taken from different plants, which are alike, and therefore exact figures concerning the composition of tar, obtained by the destructive distillation of wood, cannot be given.

Wood-tar is a burden on the hands of the wood distillers, on account of the difficulties it causes in the treatment of the pyroligneous acid, and on account of its small value as a commercial article.

The coal tar industry furnishes pitch and tar oils much cheaper and in much greater quantities than can be obtained from wood tar. The treatment of tar has therefore no great importance for the wood distiller, and usually it is limited to the recovery of the wood alcohol and acetic acid, the remaining tar compounds being, for the most part, used as fuel.

In order to recover methyl alcohol and

pyroligneous acid, contained in both varieties of tar, the tar is subjected to distillation in copper stills, provided with a heating coil and also a perforated coil for adding live steam.

The water with the acetic acid, as well as with the wood alcohol, and light wood oils floating on water, is distilled, and when by increased steam supply the amount of distillate diminishes, live steam is added by the perforated coil and the distillation continued until the distillate contains only a small amount of acids. The distillate is allowed to stand, whereby the light oils rise to the top. The clear liquid is drawn off and treated together with the distillate obtained from the bulk of the crude pyroligneous acid.

The residue of this tar distillation, or that obtained by distilling off the pyroligneous acid from the tar, is a liquid similar to thick molasses, and is generally used as fuel which is burned by spraying it by means of steam into the fireplaces of boilers or retorts. Sometimes the settled tar is subjected to distillation in order to recover the heavy tar oils, containing the phenols and creosote and to manufacture pitch. Such distillation must be carried out in cast-iron stills, heated by an open fire. First the light oils, floating on water, and the pyroligneous acid distil over, as in the process described above. This phase of the distillation must be done very carefully on account of the frothing to which the tar is liable. After this period is over and when only small amounts of water flow from the condenser, the fire can be increased, when heavy tar oils, sinking in water, distil over. The distillation will be continued until the pitch, left as a residue in the still, proves to have the melting-point desired.

Sometimes hard pitch with a high melting-point, sometimes soft pitch with a low melting-point is the purpose of this distillation.

The heavy tar oils or the oil which sinks in water are usually sold to chemical works, which manufacture creosote, and only exceptionally are they sold for the manufacture of dyes. Only a very few factories deal with the recovery of creosote, which is contained up to 1 p.c. in the hard wood tar, particularly in beech tar.

The raw material is the 'heavy tar oil' obtained by the distillation of the settled tar in fire-heated stills. These oils still contain considerable amounts of tar and must be redistilled before being subjected to any other treatment. The redistilled oils are then subjected to a systematic extraction by means of caustic soda solution, which separates the total amount of phenols from the bulk of hydrocarbons contained in the tar oils.

The alkaline solution of phenols is then mixed with acid, usually a mineral acid, liberating the phenols, which are drawn off from the salt solution, after allowing the mixture to stand. Repeated fractional distillation is the next operation to which these mixtures of phenols are subjected in order to concentrate the fractions which contain the real creosote. These fractions are again subjected to repeated treatment with caustic soda and mineral acid, and from the last fractions of the distilled creosote, 'pure' creosote is obtained.

Crude turpentine and crude pine tar. As described above, the destructive distillation of pine wood, rich in turpentine and rosin, yields the turpentine, partly in the state as originally contained in the wood, partly contaminated or mixed with the products of the destructive distillation of cellulose, lignin and rosin, *i.e.* with tar, tar oils, rosin oils, &c. The more nearly the distilling apparatus allows of a uniform distribution of heat to each piece of wood contained in the retort, the better will be the separation of the real turpentine, uncontaminated with the products above mentioned.

The destructive distillation of pine wood containing turpentine and rosin, yields three fractions, which are usually taken separately:

Fraction 1, containing only small amounts of tar, tar oils and rosin oils.

Fraction 2, containing less than 50 p.c. of the contaminating products.

Fraction 3, containing more than 50 p.c. of the contaminating products.

Fraction 1 represents the material, called 'crude wood turpentine,' which is exported from Sweden and Russia and which is also manufactured in many factories situated in the Southern States of America, as Georgia, Alabama, Virginia, &c.

The 'crude wood turpentine' obtained by destructive distillation consists principally of terpenes. In addition it contains tar, acids, phenol, aldehydes, furfural, 'silvan,' dimethylfurfural, benzene, toluene, xylene, diacetyl, acetyl-propionyl, &c.

The first treatment consists in fractionally distilling the crude wood turpentine by means of steam-heated stills, which allows also of the addition of live steam (Fig. 21), whereby the turpentine is separated from the products of lower and higher boiling-point. After the products of lower boiling-point have been got rid of, live steam is turned on and the mixture of vapours of turpentine and water is passed through caustic soda solution or milk of lime in a container connected with the still and the condenser.

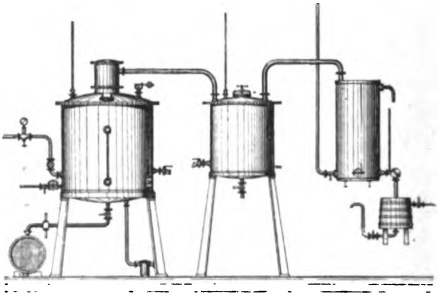


Fig. 21.

Distilling apparatus for separating turpentine from pine-wood tar-oils and pine-wood tar; type, F. H. Meyer.

Phenols, rosin oil, aldehydes, acids, &c., are kept back or destroyed by the alkaline bath, whilst the turpentine and water vapours escape to the condenser and are separated after their condensation by their varying specific gravity.

The refined turpentine obtained by this process is of a water-white colour, but its smell is not 'sweet' enough to meet the requirements of the market.

It is therefore subjected to a second alkaline treatment and then to a treatment with sulphuric acid, whereby other contaminating products will be separated or destroyed.

Finally a fractional vacuum distillation by means of steam-heated rectifiers yields a product, which is now of a water-white colour, of a 'sweet' smell, and has the same boiling-point, specific gravity, and optical characteristics as ordinary turpentine.

'Pine wood tar' is obtained as the residue of the first distillation of the crude wood turpentine.

The second fraction of the destructive distillation of pine wood, containing up to 50 p.c. tar and rosin oils, is also subjected to distillation as above described. The distillate is a mixture of turpentine, other terpenes and hydrocarbons of a higher boiling-point, called 'pine oil,' and the residue consists of pine tar.

The mixture of turpentine and pine oil is then subjected to fractional distillation by means of a vacuum rectifier and the turpentine obtained by this treatment mixed and treated together with the refined turpentine obtained from the first fraction.

The third crude fraction, mainly consisting of tar, is subjected to similar treatment and furnishes pine oils and, as a residue, the bulk of pine tar. M. K.

WOOD GUM *v.* Gums.

WOOD NAPHTHA *v.* Wood, destructive distillation of.

WOOD OIL or **GURGUN** *v.* Oleo-resins.

WOOD-PITCH, WOOD-SPIRIT, WOOD-TAR, *v.* Wood, destructive distillation of.

WOOD'S ALLOY *v.* Tin.

WOOD-TIN *v.* Cassiterite.

WOODY NIGHTSHADE *v.* Dulcamara.

WOOL. The woolly covering of the sheep is composed of modified hairs which grow in the same manner as the hairs of other animals, but differ from them considerably in physical structure and characteristics, including fineness, softness, waviness, and highly serrated surface. The wool fibre arises in the dermis or middle layer of the skin. Its root or follicle is a gland which produces a lymph-like secretion which nourishes the hair during its development and growth. This gland also secretes an oily substance, the wool-oil, which becomes a constituent part of the fibre and improves its elasticity and flexibility. Contiguous to the follicle are the sebaceous glands which secrete a fatty substance, the wool-grease, which coats the surface of the fibres, thereby protecting them from mechanical injury during growth and preventing them from becoming matted or felted together.

The dried perspiration of the animal also adheres to the fibres and can be removed by means of cold water in which it is soluble. It consists largely of a mixture of potassium salts, and is usually recovered as a by-product of the industry. The residue obtained after treating the wool with cold water and evaporating the solution to dryness is known as 'sudorate of potash.' Raw wool yields about 8 p.c. of this product.

Before the wool can be used for the manufacture of textiles, not only must the dried perspiration be removed, but also the wool-grease; the extraction of the latter is generally effected by the process of scouring with soap and water. In order to avoid the removal of the wool-oil from the interior of the fibre, the temperature at which the scouring is carried out does not usually exceed 50°.

When examined with the microscope, the typical wool fibre presents the appearance of a more or less cylindrical rod covered with irregularly-shaped scales which overlap one another by their free margins and cause the fibre to exhibit numerous serrations. The free edges of the scales always point in the direction of growth of the fibre. It is to this peculiar imbricated nature of the surface that the felting property of wool is due. The shrinking which wool fabrics undergo on washing is also attributable to the serrations; the rubbing of the material causes the projecting edges of the scales to become closely interlocked, and thus reduces the amount of space occupied by the fibres, and this behaviour is facilitated by the lubricating action of the soap. The cortical layer beneath the scales constitutes the bulk of the fibre and is composed of long, narrow cells with pointed ends. Within this is the medulla which consists of larger and rounded cells and often contains pigment to which certain wools owe their characteristic colour. In the finer wools, the medulla is often so much reduced as to be almost indistinguishable. The wool of carelessly-bred sheep frequently contains defective fibres in which the scales and cellular structure are but slightly developed; these appear as stiff, straight, coarse, opaque hairs which cannot be dyed, and are termed 'kemps.'

The value of wools and their suitability for different purposes depend very largely on their physical properties, such as length, strength, elasticity, fineness, softness, curliness or waviness, lustre, felting property, colour, and freedom from impurities and kemps. The extent to which a wool possesses these characters varies greatly with the particular breed of sheep, the climatic conditions, the nature of the pasturage, and the care exercised in selection and rearing. The quality of the fibre also varies considerably in different parts of the same fleece. The wools of commerce may be roughly divided into three classes: (1) long-stapled, (2) medium-stapled, and (3) short-stapled.

(1) The long-stapled class includes the typical English varieties, such as the Lincoln, Leicester, and Cotswold wools. The fibre is from 6 to 10 ins., or even up to 15 ins. in length, has an average diameter of about 0·001 inch, and bears from 600 to 1400 serrations per inch. It is nearly white, lustrous, of good elasticity, and has a smoother surface and less wavy character than the fibres of the other classes. The scales are horny and closely attached to the cortical layer and, in consequence, the felting power is poor. These wools are specially adapted for the manufacture of worsted yarns.

(2) The medium-stapled class is represented by the wools produced by the Southdown sheep and those of the Cheviot Hills, Shropshire, Hampshire, Oxfordshire, and Dorsetshire; it also includes certain cross-bred wools, such as those of Australia, New Zealand, and South

America, which are produced in very large quantities. The characters of the fibre are intermediate between those of the long- and short-stapled kinds. The length is from 3 to 8 ins., the average diameter about 0·0008 in., and the average number of serrations is about 2000 per inch.

(3) The short-stapled class comprises the finest grades of wool, including those of the merino type of Australia, South America, and the Cape Province of South Africa. The fibre is from 2 to 5 ins. long, has an average diameter of about 0·0005 in., and bears about 2800 serrations per inch. It is either white or of a greyish tint, has little or no lustre, and is very elastic, very soft, and curly. The scales are small and adhere to the cortical layer by only a small portion of their length, so that the upper part is free and protruding, and for this reason the wool has good felting properties. Wools of this class are particularly suitable for the manufacture of woollen fabrics.

Wool fibre is composed of a protein substance of the group known as the keratins, which also includes those derived from hair, horn, whalebone, feathers, and egg-membrane. All the members of this class differ from other proteins in yielding a large proportion of cystine on hydrolysis. The average elementary composition of wool keratin is approximately as follows: C, 51; H, 7; O, 21; N, 17; S, 4 p.c.

Sulphur is the most variable constituent and ranges from 2·5 to 4·5 p.c. Raikow (Chem. Zeit. 1905, 29, 900) found that when wool is kept for some time in contact with syrupy phosphoric acid, sulphur dioxide is evolved. Baudisch (*ibid.* 1908, 32, 620) confirmed this result and also showed that the sulphur of wool is partly oxidised to sulphur trioxide by the action of hydrogen peroxide. The experiments indicate that some of the sulphur is in direct combination with oxygen and is probably present in the form of a sulphite-like complex. This conclusion, however, has been challenged by Strunk and Priess (Zeitsch. physiol. Chem. 1912, 76, 136).

Schützenberger (Compt. rend. 1878, 86, 767) investigated the decomposition of wool keratin by solution of barium hydroxide at 170°, and found that 100 grms. of purified wool yielded nitrogen (evolved as ammonia), 5·25 grms.; carbon dioxide, 4·27 grms.; oxalic acid, 5·72 grms.; acetic acid, 3·2 grms.; pyrrole and volatile products, 1–1·5 grm.; whilst the residue consisted of leucine, tyrosine, and other nitrogenous substances.

The hydrolysis of wool keratin by hydrochloric acid was studied by Abderhalden and Voitinovici (Zeitsch. physiol. Chem. 1907, 52, 348), and it was found that various amino acids were produced in the following quantities p.c.: glycine, 0·6; alanine, 4·4; valine, 2·8; leucine, 11·5; tyrosine, 2·9; serine, 0·1; cystine, 7·3; proline, 4·4; aspartic acid, 2·3; and glutamic acid, 12·9. A comparison of these results with those obtained by the hydrolysis of the keratins of hair, horn, and feathers showed that all these substances are different, and led to the conclusion that keratin is a mixture of proteins.

Purified wool contains 1–2 p.c. of mineral constituents. The following analyses of the ash of a sample of Lincoln wool are due to Bowman. The wool, after being scoured, washed, and dried, yielded 1 p.c. of ash, of which 75 p.c. was soluble in water.

	Whole ash	Soluble ash	Insoluble ash
Potassium oxide K_2O .	31·1	42·3	trace
Sodium oxide Na_2O .	8·2	17·3	trace
Calcium oxide CaO . .	16·9	4·5	51·2
Alumina Al_2O_3 . .	13·3	3·6	37·7
Ferric oxide Fe_2O_3 . .			
Silica SiO_2 . . .	5·8	4·1	11·1
Sulphur trioxide SO_3 .	20·5	24·8	trace
Carbon dioxide CO_2 .	4·2	3·4	—
Phosphorus pentoxide P_2O_5	trace	trace	trace
Chlorine . . .	trace	trace	—
	100·0	100·0	100·0

Scoured wool usually contains about 13–14 p.c. of water. The fibre is hygroscopic and the amount of moisture present therefore varies a good deal with the state of the atmosphere. On this account, it is the custom for the moisture in a consignment of wool to be estimated before sale, and the true selling weight calculated on a certain standard percentage of moisture, the so-called 'regain.' The standard adopted at Bradford and Manchester for scoured wools is 16 p.c. of the weight of the dried fibre.

Wool is very susceptible to attack by dilute alkali hydroxide and is easily dissolved by a boiling 5 p.c. solution of sodium hydroxide. This reaction is employed for estimating the amount of wool in a material composed of a mixture of this fibre and cotton. When, however, wool is treated at the ordinary temperature with a strong solution of sodium hydroxide (sp.gr. 1·4–1·5), the fibre is not destroyed, but becomes white and lustrous, acquires a 'scroop' (the grating sound caused by rubbing the fibre) resembling that of silk, shows a greater affinity for dyestuffs, and increases in strength to an extent of about 30 p.c. Wool treated in this manner is said to be 'mercerised.' The process results in the removal of a large proportion of the sulphur; Matthews found that a sample of wool, originally containing 3·42 p.c. of sulphur, retained only 0·53 p.c. after being mercerised.

Strong solutions of potassium and sodium carbonate at high temperatures cause the disintegration of the fibre; but weak solutions at moderate temperatures are not injurious, and are extensively used in the scouring process.

By boiling purified wool with solution of barium hydroxide, removing the excess of the reagent with carbon dioxide, and adding solution of lead nitrate, a precipitate is produced which on treatment with hydrogen sulphide yields a product termed 'lanuginic acid' (Champion, Compt. rend. 1871, 72, 330). This substance has been re-examined by Knecht (J. Soc. Dyers, 1889, 71), who describes it as a brownish-yellow solid which dissolves slowly in cold water and easily in hot water. Its aqueous solution precipitates acid and basic colouring matters with formation of coloured lakes. Knecht found the substance to have the following composition: C=41·61; H=7·31; N=10·26; S=3·35; O=31·44.

Wool is completely destroyed by strong mineral acids, but is little affected by dilute acids. When heated with dilute nitric acid, the fibre assumes a permanent yellow colour. If it is warmed with dilute sulphuric or hydrochloric acid, it becomes harsher to the touch and acquires an increased affinity for dyes. The resistance of wool to the action of sulphuric acid enables it to be quantitatively estimated in a fabric composed of a mixture of wool and cotton or other vegetable fibre. The fabric is steeped for some hours in a mixture of equal volumes of concentrated sulphuric acid and water, with the result that the vegetable fibre is destroyed, whilst the wool is not attacked and can be collected, washed, dried, and weighed.

Nitrous acid seems to diazotise the amino groups of wool keratin. Wool which has been treated with this reagent is harsh to the touch, non-hygroscopic, and assumes various colours when brought into contact with alkaline solutions of certain phenols.

Wool is very little affected by dry chlorine, but is decomposed by the gas in presence of moisture. The fibre is capable of absorbing chlorine from weak solutions and becomes harsh, acquires a 'scroop,' loses its felting properties, thus becoming 'unshrinkable,' and also acquires an increased affinity for colouring matters.

For further information, reference should be made to Bowman's Structure of the Wool Fibre, or to Matthews' Textile Fibres. E. G.

WOOL BLACK, *v.* Azo- colouring matters.

WOOL OILS. Under the trade term 'wool oils' or 'cloth oils' are comprised all those oils that are used by woollen manufacturers for lubricating the wool before spinning, or for oiling the rags before 'grinding' and 'pulling.'

The best wool oils consist of pure fatty oils, such as olive oil, lard oil, neat's foot oil. Besides these, oleic acid ('saponification oleine' or 'saponified oleine,' 'distillation oleine' or 'distilled oleine' (*see* Saponification)) is used largely as a cheaper kind of wool oil.

The tendency to produce cheap wool oils, especially those for use with the lowest textile goods, has led to the employment of 'distilled grease oleine,' and even 'waste oils,' such as 'black recovered oil,' 'seek oil,' and 'brown grease oil.' The last-named oils contain considerable amounts of unsaponifiable matter. Besides these oils there are found in commerce large quantities of 'manufactured oils,' representing blends of the above-named wool oils, as also blends containing mineral oils. For the examination of wool oil *see* Lewkowitsch, Chem. Techn. iii. 77. J. L.

WOOL SCARLET *v.* Azo- colouring matters.

WOOTZ. An Indian name for steel.

WORMSEED *v.* Santonica.

WORMSEED, OIL OF, *v.* Oils, essential.

WORMWOOD. The leaves and tops of *Artemisia Absinthium* (Linn.) contain a volatile oil, *absinthol* (*q.v.*) and a bitter principle, *absinthin* (*q.v.*). Wormwood is a bitter stomachic tonic, and is used in medicine as a remedy for atonic dyspepsia, and as an anthelmintic.

WORT *v.* Brewing.

WOURALI, WOURARA, WOURARI *v.* Curara.

WULFENITE (*Gelbbleierz Molybdänbleispat*, Ger.). A mineral consisting of lead molybdate $PbMoO_4$ crystallising in the tetragonal system (hemimorphic-tetratohedral class) and isomorphous with scheelite (*q.v.*). Next to molybdenite (*q.v.*) it is the most abundant of the few minerals containing molybdenum. It has been found in some quantity at Bleiberg in Carinthia, and at several places in Arizona, Nevada, and Utah, often as beautifully crystallised specimens of rich yellow or red colours. L. J. S.

WURTZITE. A native form of zinc sulphide (ZnS) crystallising in the hexagonal system, and thus dimorphous with the more common cubic mineral blende (*q.v.*). It was described from Oruro in Bolivia by C. Friedel, and named after the French chemist C. A. Wurtz (1817–1884). Crystals are hemimorphic and very like those of zincite (ZnO, *q.v.*); but, as a rule, the mineral forms fibrous masses. Much fibrous and shelly blende which is optically birefringent, and known by the names 'spiauterite' and 'Schalenblende,' really belongs to this species; and it sometimes, no doubt, forms an important part of massive zinc sulphide ore. The phosphorescence shown by the mineral when struck has often been observed by miners. The hexagonal zinc sulphide used for coating phosphorescing screens in Röntgen ray work is the artificially prepared material. This was first obtained by J. Durocher in 1851, by E. H. Sainte-Claire Deville and L. Troost in 1861, and more successfully by T. Sidot in 1866 (Compt. rend. 62, 999; 63, 188). Sidot obtained long, colourless and transparent, hexagonal prisms by subliming blende in a current of sulphur dioxide.

L. J. S.

X

XANTHEIN. The name applied by Fremy and Cloez to the soluble yellow colouring matter of flowers.

XANTHENE COLOURING MATTERS, a name sometimes applied to the dyestuffs containing the group  and including the *pyronines*, colouring matters and triphenylmethane colouring matters (*q.v.*).

XANTHIC ACIDS (*Alkyloxydithiocarbonic acids*) RO·CS·SH, may be prepared by dissolving sodium in the required pure dry alcohol and adding the calculated quantity of dry carbon disulphide, the mixture being stirred and cooled. In this way a sodium xanthate is formed, which, on treatment with dilute sulphuric or hydrochloric acid, yields the free xanthic acid (Ragg, Chem. Zeit. 1908, 32, 630, 654, 677; *ibid.* 1910, 34, 82).

Xanthic acid (*ethoxydithiocarbonic acid*) is a colourless, transparent, heavy oil, insoluble in water and decomposing at 24° into alcohol and carbon disulphide. It forms a large number of metallic salts. The sodium or potassium salts when treated with a copper salt yield *cuprous xanthate* and *ethyldioxythiocarbonate* (*dixanthogen*) thus:

$$4NaS{\cdot}CS{\cdot}OEt+2CuSO_4 \\ =Cu_2(S{\cdot}CS{\cdot}OEt)_2+S_2(CS{\cdot}OEt)_2+2Na_2SO_4.$$

The cuprous salt is yellow, and it is this reaction which led to the adoption of the name for these salts. When the metallic xanthates are heated to 350° they decompose with evolution of hydrogen sulphide, carbon dioxide, and small quantities of combustible gases containing carbon monoxide. Amongst the liquid products are carbon di- and oxy-sulphide, ethyl hydrogen sulphide, ethyl mono- and disulphide, and ethyl alcohol, but in the case of the silver and nickel salts, the liquid product consists of almost pure ethyl xanthate and the dry distillation of the nickel salt is recommended for the preparation of the ethyl salt (Hébert, Compt. rend. 1911, 152, 869).

Potassium propylxanthate has been proposed as a reagent for cobalt and nickel salts; with the latter it yields a yellow precipitate, whilst with the former a green precipitate is formed. In dilute solutions the nickel is precipitated before the cobalt. Potassium methyl xanthate is also a good reagent giving with nickel a soluble, with cobalt an insoluble, salt in ammonia (Ferrer Hernández and Campo y Cerdan, Anal Fis. Quim. 1911, 9, 173).

When sodium or potassium alkyl xanthate is treated with chloracetyl carbamides, the following products are obtained: chloracetyl carbamates, arylamines, xanthylacetyl carbamides, ethyl carbamates, and arylamides (Frerichs and Rentschler, Arch. Pharm. 1906, 244, 77).

The esters of xanthic acid and its homologues may be obtained by treating the alkali salts with alkyl halide. They are volatile liquids which react with alkali alkoxides thus:

$$RO{\cdot}CS_2{\cdot}R+R'OK+H_2O \\ =R'O{\cdot}CO{\cdot}SK+R{\cdot}OH+R{\cdot}SH$$

(Salomon, Ber. 1875, 8, 1507; Wallach, *ibid.* 1880, 13, 530).

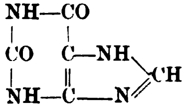
When treated with ammonia they yield mercaptan and *xanthamides* (alkylthiocarbamates) $RO{\cdot}CS{\cdot}NH_2$. The *ethyl salt*

$$C_2H_5O{\cdot}CS{\cdot}NH_2,$$

which is known as *xanthamide*, has m.p. 40°–41° (Debus, Annalen, 1850, 75, 128; *ibid.* 1852, 82, 262; Salomon, J. pr. Chem. 1874, [ii.] 8, 115; Rosenheim and Stadler, Zeitsch. anorg. Chem. 1906, 49, 1).

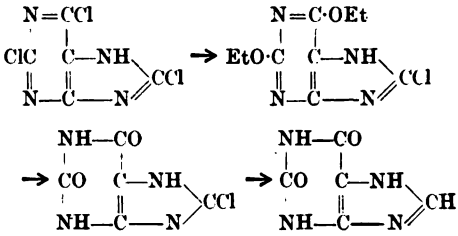
Xanthic derivatives of certain carbohydrates such as starch, have been prepared by first saturating the dry powdered carbohydrate with carbon disulphide and then adding the required quantity of caustic soda solution (Fr. Pat. 370505, 1906; J. Soc. Chem. Ind. 1907, 267). For other literature, *see* Tschugaeff, Ber. 1900, 33, 735; Bull. Soc. chim. 1901, [iii.] 26, 184, 298, 502; Leuckart, J. pr. Chem. 1890, [ii.] 41, 179; Holmberg, *ibid.* 1905, [ii.] 71, 264; Biilmann, Annalen, 1906, 348, 133.

XANTHINE, 2:6-dioxypurine



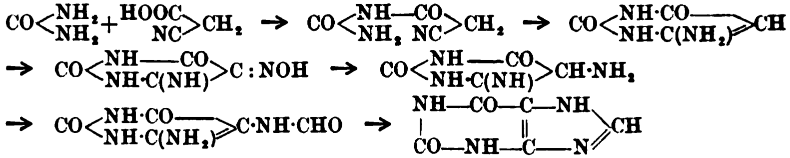
was discovered in 1817 by Marcet in a urinary calculus and called 'xanthic oxide,' because of the yellow residue it left when evaporated to dryness with nitric acid. Wöhler and Liebig analysed the compound, which they isolated from another calculus, and found that it differed from uric acid in containing one atom of oxygen less in the molecule (Annalen, 1838, 26, 340). It occurs in guano (Strecker, *ibid.* 1861, 118, 157), to a small extent in urine, 10,000 litres contain 10·11 grms. (Krüger and Salomon, Zeitsch. physiol. Chem. 1898, 24, 371; 26, 367); in the muscles, liver, spleen, pancreas, thymus and brain (Micko, Zeitsch. Nahr. Genussm. 1903, 6, 781; 1904, 7, 257). It is also found in the actively growing tissues of plants, in yeast, tea, and seedlings of lupins and malt; and has been isolated, together with other purine bases, from the soil (Schreiner and Shorey, J. Biol. Chem. 1910, 8, 385).

Synthesis. Xanthine can be prepared by heating 2:6:8-trichloropurine with sodium ethoxide, and reducing the 2:6-diethoxy-8-chloropurine either directly by hydrogen iodide, or after preliminary hydrolysis, to 2:6-dioxy-8-chloropurine (Fischer, Ber. 1897, 30, 2232).



Xanthine is also obtained by heating 2:6-di-iodopurine with hydrochloric acid under pressure (Fischer, *ibid.* 1898, 31, 2550). Traube (*ibid.* 1900, 33, 1371, 3043) has effected the synthesis of xanthine from cyanacetyl urea; this is converted by the action of alkalis into 4-amino-2:6-dioxypyrimidine which, by the action of nitrous acid and subsequent reduction, yields 4:5-diamino-2:6-dioxypyrimidine: on heating the sodium salt of the formyl derivative of this compound, xanthine is obtained (see scheme at top of next page).

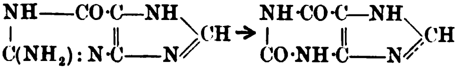
When uric acid is reduced by nascent formic acid, it yields xanthine. This may be effected by heating a mixture of uric acid, formic acid, chloroform, and alkali on the water bath; or by heating a mixture of equal weights of uric acid, calcium formate and calcium hydroxide in a combustion furnace until evolution of gas begins; or, more simply and with a yield of 30–33 p.c., by heating at 200° uric acid mixed



with oxalic acid and excess of glycerol (Sundvik, Zeitsch. physiol. Chem. 1897, 23, 476; 1898, 26, 131; 1912, 76, 486; Skan. Arch. Physiol. 1911, 25, 256).

The following technical preparation of xanthine from thioxanthine is described by C. F. Boehringer and Soehne, D.R.PP. 141974, 142468, 143725. An alkaline solution of *iso*uric acid absorbs sulphuretted hydrogen, forming a salt of γ-thio-ψ-uric acid, which is converted by boiling with mineral acids into thioxanthine (2:6-dioxy-8-thiopurine); or the thioxanthine may be prepared by warming 4:5-diamino-2:6-dihydroxypyrimidine with carbon disulphide and potassium hydroxide. On oxidising thioxanthine by means of nitrous acid, hydrogen dioxide in alkaline solution or manganese dioxide in neutral solution, it is converted into xanthine.

Xanthine is most conveniently prepared from guanine by the action of nitrous acid, or more readily and with a yield of 60–70 p.c. by heating in a reflux apparatus for 32 hours with 25 p.c. hydrochloric acid (Fischer, Ber. 1910, 43, 805)



Properties. Xanthine crystallises with one molecule of water which it loses at 125°–130°, forming a colourless micro-crystalline powder that acquires a waxy lustre by friction (Wöhler and Liebig, *l.c.*); it dissolves in 14,151 parts of water at 16° or 1300–1500 parts at 100°, and is insoluble in alcohol or ether. It dissolves readily in solutions of sodium or potassium hydroxides or in ammonia, but is precipitated from the solution by acids, even carbon dioxide. Xanthine sublimes slightly when heated, but decomposes without melting, yielding carbon dioxide, ammonia, hydrocyanic acid and cyanogen.

Xanthine is oxidised by chlorine oxides or chlorine water, yielding alloxan and urea (Fischer, Annalen, 1882, 215, 253).

Detection and estimation. Xanthine gives the murexide reaction when evaporated to dryness with chlorine water or hydrochloric acid and potassium chlorate and the residue moistened with ammonia solution; this is commonly called 'Weidel's test' for xanthine, although this author described it as a test for *hypoxanthine* (Annalen, 1871, 158, 365), and Kossel showed that the reaction was due to the presence of *xanthine*, pure *hypoxanthine* not responding to the test (Zeitsch. physiol. Chem. 1882, 6, 431).

Xanthine dissolves in hot nitric acid without evolution of gas, and the yellow residue obtained on cautious evaporation of the acid solution turns reddish-yellow on addition of sodium or potassium hydroxide and changes to reddish-violet on heating. If ammonia be used instead the alkali hydroxides, no violet colour is produced, and this test distinguishes xanthine from uric acid which gives the murexide reaction when similarly treated.

If dry xanthine be sprinkled on an alkaline solution of bleaching powder, each particle becomes surrounded with a dark green ring or scum which quickly changes to brown and finally disappears. Xanthine develops a red colour when added to an alkaline solution of diazobenzenesulphonic acid.

Xanthine can be estimated by precipitating the insoluble silver compound by means of silver nitrate from an ammoniacal solution, and estimating the nitrogen present in the carefully washed precipitate by the Kjeldahl method; or the silver may be estimated gravimetrically or volumetrically.

For the separation of xanthine from the purine bases in urine or extract of tissues, see Abderhalden's Handbuch der Biochemischen Arbeitsmethoden, vol. iii. part 2, p. 894.

Salts and derivatives. Xanthine forms compounds with certain metallic oxides and salts, the compound with *silver oxide*

$$C_5H_4O_2N_4\cdot Ag_2O$$

is a flocculent precipitate obtained by precipitating an ammoniacal solution of xanthine with ammoniacal silver nitrate; with *silver nitrate* $C_5H_4O_2N_4\cdot AgNO_3$ a flocculent precipitate prepared by mixing a nitric acid solution of xanthine with silver nitrate solution; the compound with *lead* $C_5H_2O_2N_4Pb$ is white and crystalline; and the compound with *barium hydroxide* $C_5H_4O_2N_4\cdot Ba(OH)_2$ is sparingly soluble. Xanthine forms crystalline salts with the mineral acids which are generally readily hydrolysed by solution in water; the *sulphate*

$$C_5H_4O_2N_4\cdot H_2SO_4,H_2O$$

crystallises in pearly rhombic plates from hot strong sulphuric acid, or in microscopic needles from dilute acid; the *hydrochloride*

$$C_5H_4O_2N_4\cdot HCl$$

crystallises in warty masses; the *nitrate* $C_5H_4O_2N_4\cdot HNO_3$ is precipitated as a heavy crystalline powder, when a warm solution of xanthine in sodium hydroxide is added to a cold solution of nitric acid (2:3); the *periodide* $C_5H_4O_2N_4\cdot HI\cdot I_3$ forms characteristic green crystals from alcohol (Linarix, J. Pharm. Chim. 1909, [vi.] 30, 241).

Xanthine-7-diazobenzensulphonic acid

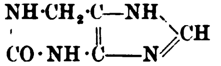
$$(C_5H_3O_2N_3)N\cdot N:N\cdot C_6H_4\cdot SO_3H$$

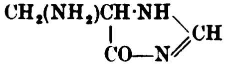
dark red crystalline needles that do not decompose at 265°, soluble in water or alkalis, insoluble in ether, sparingly soluble in alcohol (Burian, Ber. 1904, 37, 703).

8-*Chloroxanthine* $C_5H_3ClO_2N_4$, obtained by hydrolysing 2:6-diethoxy-8-chloropurine with hydrochloric acid, forms a sparingly soluble crystalline powder that blackens without melting when heated (Fischer, Ber. 1887, 30, 2236).

8-*Bromoxanthine* $C_5H_3BrO_2N_4$ obtained by direct bromination at 100°, or by the action of nitrous acid on bromoguanidine; is a crystalline powder, insoluble in cold, sparingly soluble in hot water, insoluble in alcohol or ether, and decomposes without melting (Fischer and Reese, Annalen, 1883, 221, 343).

8-*Thioxanthine* $C_5H_3(SH)O_2N_4$, obtained by heating 8-bromoxanthine with potassium hydrogen sulphide solution in a sealed tube at 120° (Fischer, Ber. 1898, 31, 433), or by methods already referred to in the description of the synthesis of xanthine: is a colourless heavy crystalline powder that blackens without melting on being heated, sparingly soluble in concentrated hydrochloric acid and readily soluble in alkalis.

Deoxyxanthine 
$$\begin{array}{l}NH\cdot CH_2\cdot C—NH\diagdown \\ \quad\quad\quad\quad\quad\ \| \quad\quad\quad\ \ \ >CH \\ CO\cdot NH\cdot C—N\diagup\!\!\diagup\end{array}$$
obtained by the electrolytic reduction of xanthine dissolved in sulphuric acid, using lead electrodes; forms colourless crystals that decompose without melting after becoming brown at 250° (Tafel and Ach, Ber. 1901, 34, 1166). It is very readily hydrolysed when gently heated with acids, yielding carbon dioxide, ammonia and 5-aminomethyl-4-iminazolone


$$\begin{array}{l}CH_2(NH_2)CH\cdot NH\diagdown \\ \quad\quad\quad\ \ | \quad\quad\quad\quad >CH \\ \quad\quad\quad CO—N\diagup\!\!\diagup\end{array}$$

(Tafel and Mayer, Ber. 1908, 41, 2546).

M. A. W.

XANTHINE (CHRYSANILINE) *v.* ACRIDINE DYESTUFFS.

XANTHOCREATININE, CRUSOCREATININE and **AMPHICREATININE** are the chief members of the creatinine leucomaines isolated by Gautier from the muscles of large animals; they are alkaloidal in properties, and when administered to animals act more or less powerfully on the nerve centres inducing sleep, and in some cases vomiting and purging in a manner similar to the alkaloids of snake poison. These bases are formed during life and occur in the urine, saliva, and various glandular secretions (J., Pharm. Chim., [v.] 13, 354, 401).

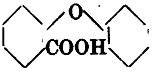
Xanthocreatinine $C_5H_{10}ON_4$ is the most abundant of the creatinine leucomaine group of bases. It was extracted from muscle by Gautier and also by Monari (Gazz. chim. ital. 1887, 16, 538) and from the urine of the lion by Colosanti (*ibid.* 21, ii. 188). In chemical properties it closely resembles creatinine from which it differs in empirical constitution by CH_3N. It crystallises in light sulphur-yellow spangles, which have a slightly bitter taste and an odour similar to that of crude acetamide. The base is soluble in cold water and can be crystallised from boiling alcohol. It is amphoteric in character, turning blue litmus red and red litmus blue. It forms a salt with hydrochloric acid which yields soluble crystalline double salts, with the chlorides of gold, platinum, mercury and zinc. The latter compound has the formula

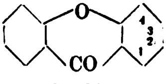
$$(C_5H_{10}N_4O)_2ZnCl_2.$$

Crucocreatinine $C_5H_8ON_4$, crystallises in orange-yellow crystals, is feebly alkaline towards litmus paper and has a slightly bitter taste. It forms a crystalline non-deliquescent hydrochloride, which yields crystalline double salts with platinic, auric and zinc chlorides respectively.

Amphicreatinine $C_9H_{19}O_4N_7$ crystallises from boiling water in bright, pale yellow prisms and is less readily soluble than either of the two preceding bases. When heated at 110° the crystals become colourless and opaque without, however, changing their form. It forms a crystalline *hydrochloride*. The *platinochloride* is soluble in water, and insoluble in alcohol and crystallises in lozenge-shaped plates, and the *aurichloride* is very readily soluble and crystallises in microscopic hexhahedral and tetrahedral crystals.

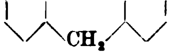
XANTHONE AND XANTHONE COLOURING MATTERS. *Xanthone, Diphenyleneketone oxide, Benzophenone oxide, Carbonyldiphenylene oxide,* $C_{13}H_8O_2$, was first prepared by Kolbe and Lautemann (Annalen, 1860, 115, 197) by the action of phosphorus oxychloride on sodium salicylate, and has been subsequently obtained from salicylic acid and its derivatives by the employment of various dehydrating agents. The most convenient method consists in distilling a mixture of acetic anhydride and salicylic acid (Perkin, Chem. Soc. Trans. 1883, 43, 35; *cf.* also Graebe. Annalen, 254, 265), when the higher boiling fraction, on cooling, deposits crystals of xanthone. Phenyl salicylate (Siefert, J. pr. chem. [ii.] 31, 472) by long digestion at the boiling temperature yields xanthone, and it is also produced when salicylic acid phenylether $COOH\cdot C_6H_4\cdot O\cdot C_6H_5$ is warmed with sulphuric acid (Graebe, Ber. 21, 503). Other methods of this type have been described by Richter (J. pr. chem. [ii.] 28, 275), Jeiteles (Monatsh. 17, 66), Staedel (Annalen, 283, 179), Goldschmiedt (Monatsh. 4, 123). and Klepl (J. pr. chem. [ii.] 28, 217). For the theory of xanthone formation the paper of Strohbach (Ber. 34, 4136) should be consulted. Ullmann and Zlokasoff (*ibid.* 1905, 2111), by the interaction of sodium phenoxide and sodium *o*-chlorbenzoate in presence of copper powder, obtained *o*-phenoxybenzoic acid (1) which, by elimination of water, passes into xanthone (2).

(1) 

(2) 

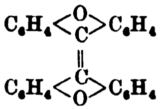
and this method is generally applicable for the production of xanthone derivatives.

Xanthone crystallises in long colourless needles, m.p. 173°–174°, and dissolves in sulphuric acid to form a blue fluorescent liquid. By distillation with zinc dust or by the action of fuming hydriodic acid at 160°, it is converted into *xanthene* (methylene diphenylene oxide)



from which by oxidation with chromic acid, xanthone can be reproduced (Merz and Weith, Ber. 14, 192). Boiling alcoholic soda and zinc dust gives *xanthydrol* (Meyer and Laub, Ber. 26, 1276),

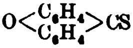
zinc dust and acetic acid *dioxyxanthylene* (Gurgenjanz and v. Kostanecki, Ber. 28, 2310),



$$C_6H_4{<}\overset{O}{\underset{C}{}}{>}C_6H_4 \;\; \| \;\; C_6H_4{<}\overset{C}{\underset{O}{}}{>}C_6H_4$$

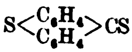
whereas by fusion with alkali *xanthonic acid* (dihydroxydiphenylene ketone) $CO(C_6H_4(OH))_2$ is obtained.

a-Dinitro-xanthone, m.p. 190° (Richter, *l.c.*; Graebe, *l.c.*), *b-dinitroxanthone*, m.p. 262° (Perkin, Chem. Soc. Trans. 43, 189), *a-diamino-xanthone*, m.p. 209 (G), *b-diaminoxanthone* (P), *xanthonedisulphonic acid* (P.), *monobromxanthone*, m.p. 125°–127° (G.), *dibromxanthone*, m.p. 212° (P.), *thioxanthone*, m.p. 209° (Graebe and Schultess, Annalen, 263, 8), *xanthone phenylimine*, m.p. 134°–135° (Graebe and Röder, Ber. 32, 1689), *xanthoneoxime* (G. and R.), *xanthione*, m.p. 156° (G. and R.)



$$O{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}CS$$

and *dithioxanthone*



$$S{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}CS$$

(Meyer and Szanecki, Ber. 33, 2580) have been described.

Special interest is attached to the hydroxyxanthones in that certain natural representatives, euxanthone and gentisin, are included in this group. A general method for the preparation of these compounds consists in distilling a mixture of a phenol, and an *o*-hydroxycarboxylic acid with acetic anhydride, and this has been employed in numerous syntheses. In this manner 1-*hydroxyxanthone* (Michael, Amer. Chem. Soc. 5, 91; Graebe, Annalen. 54, 290), m.p. 146°–147°, 2-*hydroxyxanthone* (v. Kostanecki and Rutishauser, Ber. 25, 1648), m.p. 231°, 4-*hydroxyxanthone* (K. and R.), m.p. 224°, 3-*hydroxyxanthone* (v. Kostanecki and Nessler, Ber. 24, 3981), m.p. 242°, 3:6:*dihydroxyxanthone* (iso*euxanthone*) (v. Kostanecki, *ibid.* 18, 1986), m.p. 243°, 2:5-*dihydroxyxanthone* (v. Kostanecki, *ibid.* 27, 1991), m.p. 280°, *gentisein* (1:3:7-trihydroxyxanthone) (v. Kostanecki, Monatsh. 12, 207), and *euxanthone* (3:5-dihydroxyxanthone) (v. Kostanecki and Nessler, Ber. 24, 3983) can be prepared. Whereas euxanthone is the colouring matter of Indian yellow, gentisein monomethyl ether is identical with the gentisin of gentian root (see articles). According to Tschirch and Polacco (Arch. Pharm. 1900, 238, 459), rhamnocitrin, a yellow colouring matter which is present in the berries of the *Rhamnus cathartica* (L.) is probably a trihydroxydihydroxanthone (see article Persian Berries). For the preparation of euxanthone see also Ullmann and Panchaud (Annalen, 350, 108). A. G. P.

XANTHORHAMNIN *v.* Glucosides; Persian berries.

XANTHORRHŒA RESINS or **BALSAMS** *v.* Balsam.

XENON. Sym. X. At.wt. 130·2.

An inert gas, discovered along with krypton in the final residues obtained after evaporating considerable quantities of liquid air (Ramsay and Travers, Proc. Roy. Soc. 1898, 63, 405). For the separation of xenon from these residues, *v.* Krypton. Xenon may also be separated by passing a current of air through a spiral tube filled with glass wool and immersed in liquid air (Dewar, *ibid.* 1901, 68, 360). Xenon occurs in the gases evolved from many thermal springs (Moureu and Lepape, Compt. rend. 1909, 149, 1171).

Xenon is the least volatile and least abundant of the inert gases which exist in the atmosphere, being present only to the extent of 1 part in 170 million parts of air by volume (Ramsay, Proc. Roy. Soc. 1903, 71, 421; 1908, 80, A. 599). It boils at −109·1°, at which temperature its density is 3·063 and its atomic volume 42·7. The critical temperature is +16·6°, the critical pressure 58·2 atmospheres, and the critical density 1·115 grms. per c.c. The 'rectilinear diameter' is given by the equation

$$D_t = 1{\cdot}205 - 0{\cdot}003055t$$

where D_t = mean density of liquid and saturated vapour at t° C. (Patterson, Cripps and Whytlaw-Gray, Proc. Roy. Soc. 1912, A, 579). At the temperature of liquid air xenon readily solidifies (Ramsay and Travers, Proc. Roy. Soc. 1901, 67, 329).

At N.T.P. 1 litre of xenon weighs 5·851 grms.; its density is therefore 65·35 (O=16) (Moore, Chem. Soc. Trans. 1908, 93, 2181; Watson, *ibid.* 1910, 97, 833). The refractive index at N.T.P. for the green mercury line (λ=5461) is 1·0007055 (Cuthbertson and Cuthbertson, Proc. Roy. Soc. 1908, 81, A, 440; 1910, 84, A, 13). At 20° the absorption coefficient is 0·1109 (Antropoff, *ibid.* 1910, 83, A, 474). For the spectrum of xenon *v.* Baly, (Phil. Trans. 1903, A, 202, 183): Liveing and Dewar (Proc. Roy. Soc. 1901, 68, 389).

Xenon is monatomic since the ratio of its specific heats is 1·66 (Ramsay).

XEROFORM. Trade name for bismuth tribromophenoxide used as an antiseptic, *v.* Bismuth, organic compounds of; Synthetic drugs.

XYLENES, *Dimethylbenzenes*,

$$C_8H_{10} \text{ or } C_6H_4(CH_3)_2.$$

A hydrocarbon of the formula C_8H_{10} (in reality a mixture) was obtained by various investigators from the fraction of coal-tar, or of wood-tar, boiling between 137·5°–142°. De la Rue and H. Müller isolated a similar substance from Rangoon tar. Fittig (Annalen, 1870, 153, 265) showed that the crude xylene from coal tar contained two isomeric hydrocarbons—*m-xylene*, which he had previously obtained by distilling mesitylenic acid

$$C_6H_3(COOH)(CH_3)_2(1{:}3{:}5)$$

with lime; and *p-xylene*, which he had prepared by the action of sodium on a mixture of crude bromotoluene and methyl iodide; this was first prepared in a purer form by Jannasch (Annalen, 1874, 171, 79), by employing pure *p*-bromtoluene in the same reaction. *o-Xylene* was first isolated from coal-tar by Jacobsen (Ber. 1877, 10, 1010), but had previously been obtained by Fittig and Bieber (Annalen, 1870, 156, 239) by the distillation of *p*-xylic acid $C_6H_3(COOH)(CH_3)_2(1{:}3{:}4)$ with lime.

Crude coal-tar xylene, containing paraffins and other hydrocarbons, was formerly used only as solvent naphtha. At present, purified xylene is employed in the manufacture of xylidine scarlet and other azo- colours.

The xylenes are formed, like other methyl homologues of benzene, by the decomposition of complex organic substances by heat, hence their occurrence in coal-tar and wood-tar. The *m*- compound is formed in the largest quantity; but the relative proportion of the three isomerides varies both with the material distilled and with the temperature at which the distillation is conducted. In like manner xylenes are formed, together with other hydrocarbons, when the vapour of oil of turpentine is passed through a red-hot tube. *O*-xylene, with about 5 p.c. of para-xylene, is formed when methyl chloride is passed into warm toluene containing aluminium chloride. The xylenes are also formed by the distillation of the dimethylbenzoic acids with lime.

In order to separate the isomerides, a commercial xylene, boiling at about 140°, and freed from phenols and bases by treatment with alkali and acid, is employed as the starting-point. If only the *m*- compound, which alone is of technical importance, is required, the mixture is boiled with dilute nitric acid (1 part of commercial acid of sp.gr. 1·4 with 2 parts of water); the *o*- and *p*- compounds are thus converted into acids, whilst the *m*- compound is hardly attacked (Fittig and Velguth, Annalen, 1868, 148, 10). The product is steam-distilled, the distillate shaken with alkali to free it from acids and nitro-xylenes, dried, and rectified.

O. Jacobsen (Ber. 1877, 10, 1013; 1878, 11, 17) has described a method by which the three isomerides may be isolated from coal-tar xylene. The crude xylene is shaken in the cold with concentrated sulphuric acid, which dissolves *o*- and *m*-xylene, converting them into sulphonic acids, whereas *p*-xylene is hardly attacked, even on heating. In order to obtain the *o*- and *m*-xylene, the acid solution is treated with excess of calcium carbonate, filtered from calcium sulphate, the filtrate, containing the calcium sulphonates, precipitated with sodium carbonate, and the solution of the sodium xylene-sulphonates concentrated by evaporation and allowed to crystallise. Sodium *o*-xylene-sulphonate separates, whilst the sodium salts of two isomeric *m*-xylene-sulphonic acids remain in solution. In order to purify the *p*-xylene, it is gently warmed with fuming sulphuric acid, in which it dissolves, leaving behind a paraffin and other impurities. The three xylenes are then liberated from their sulphonic acids by hydrolysis with concentrated hydrochloric acid at 195° (*see* also Armstrong and Miller, J. Chem. Soc. 1884, 151; Levinstein, J. Soc. Chem. Ind. 1884, 354).

The hydrocarbons may, of course, also be regenerated from the sulphonic acids by the dry distillation of the ammonium salts alone, or of the other salts with dry ammonium chloride.

A somewhat modified form of Jacobsen's separation which may also be employed for estimating the relative quantities of the isomerides in the mixture is described by Crafts (Compt. rend. 1892, 114, 1110; *see* also Eng. Pat. 8665, 1898).

Noelting and Palmer (Ber. *1891, 24, 1955*) have shown that commercial xylene contains ethylbenzene, and that in Jacobsen's method of separating the isomerides the *p*-xylene is obtained mixed with this hydrocarbon (*see* also Moore and Roaf, Proc. Roy. Soc. 1905, B, 77, 80; Ward, Proc. Cambridge Phil. Soc. 1905, 13, 81; Stohmann, J. pr. Chem. 1887, [ii.] 35, 41).

Commercial xylene should have been previously washed with sulphuric acid, and should, therefore, give only a pale-brown colouration on treatment with concentrated sulphuric acid. The boiling-point of the product should lie within a few degrees; thus not more than 10 p.c. should distil below 138°, and not more than 10 p.c. above 140·5°, the remainder passing over between these two temperatures.

The xylene of commerce is a product of very variable composition. The relative proportion of the three isomerides varies in different samples, and as these three compounds have almost identical boiling-points, the boiling-point of such a mixture affords no clue to its composition. The value of a commercial xylene depends on the quantity of *m*-xylene which it contains.

To identify the *m*- and *p*-xylenes in a mixture of the three isomerides, 50 c.c. of the mixture may be heated with a mixture of chromic and sulphuric acids, whereby *o*-xylene is completely oxidised to carbon dioxide, whereas *m*-xylene yields *iso*-phthalic acid and *p*-xylene yields terephthalic acid (Worstall and Burwell, Amer. Chem. J. 1897, 19, 830).

Methods for the quantitative estimation of the three xylenes in the commercial product have been devised (*v.* Levinstein, *l.c.*; Reuter, Ber. 1884, 2028; and J. Soc. Chem. Ind. 1884, 626; *ibid.* 1889, 874; Chem. Zeit. 13, 830; Crafts, *l.c.*).

When the xylenes are oxidised with chromic acid in the presence of acetic anhydride and sulphuric acid, the corresponding tetra acetate of phthalaldehyde is formed (Thiele and Winter, Annalen, 1900, 311, 353).

The xylenes and similar coal-tar hydrocarbons may be rendered soluble in water by heating them with a suitable soap, as, for instance, with oleic acid and potash. The products which are soluble both in ordinary and in sea water may be used for washing and other purposes such as drilling, turning, and similar processes in the working of metals (Fr. Pat. 422963, 1910; J. Soc. Chem. Ind. 1911, 610).

Xylene has also been employed in the removal of naphthalene stoppages in pipes (Breitkopf, J. Gasbeleucht. 1899, 42, 671).

Like the other homologues of benzene, xylene reacts with cellulose forming desoxyns (Nastukoff, Zeitsch. Farb. Ind. 1907, 6, 70).

***ortho*-Xylene** $C_6H_4(CH_3)_2$. Liquid, boiling at 144° (corr.), m.p. −25° (Fischer, Zeitsch. Elektrochem. 1910, 16, 161), sp.gr. 0·8903 at 4°/4°: sp.gr. 0·8818 at 15°/15°. Oxidised by dilute nitric acid to *o*-toluic acid

$$C_6H_4(CH_3)(COOH),$$

melting at 102°. A hot solution of potassium permanganate oxidises it to *o*-toluic and phthalic acids, whilst chromic acid totally destroys it. When heated with hydrogen iodide at 250°–280° *o*-xylene yields toluene, methyl- and dimethyl*cyclo*hexane, and methylated pentamethylene (Markownikow, Ber. 1897, 30, 1218).

m*-Xylene** (iso*-xylene**) $C_6H_4(CH_3)_2$. Liquid, boiling at 139° (corr.); m.p. −50° (Fischer, *l.c.*); sp.gr. 0·8779 at 4°/4°: sp.gr. 0·8691 at 15°/15°. Not attacked by dilute nitric acid. Chromic acid oxidises it to *iso*phthalic acid. When warmed with concentrated nitric acid it yields a trinitro derivative $C_6H(CH_3)_2(NO_2)_3$, melting at 176°, very sparingly soluble in alcohol.

For its reaction with aluminium chloride, *see* Anschütz, Annalen, 1886, 235, 182, 323; Heise and Töhl, *ibid.* 1892, 270, 169; Jacobsen, Ber. 1885, 18, 342; also Boeseken, Rec. trav. chim. 1905, 24, 1.

***p*-Xylene** $C_6H_4(CH_3)_2$. Monoclinic prisms, m.p. +5° (Fischer, *l.c.*), +15° (Jannasch, Annalen, 1874, 171, 80), b.p. 138·5°; sp.gr. 0·8661 at 15°/15°; sp.gr. 0·8593 at 25°/25°. Dilute nitric acid oxidises it to *p*-toluic acid

$$C_6H_4(CH_3)(COOH),$$

melting at 178°; chromic acid to terephthalic acid.

When *p*-xylene is heated with sulphur at 250°–300°, 4 : 4′-dimethylstilbene and 4 : 4′-dimethyldibenzyl are formed (Aronstein and Nierop, Proc. K. Akad. Wetensch. Amsterdam, 1902, 5, 288; Rec. trav. chim. 1902, 21, 448).

Halogen derivatives. The bromo and dibromo derivatives of all three xylenes may be obtained by direct bromination of the hydrocarbon, the product obtained depending on the conditions of the experiment (Atkinson and Thorpe, Chem. Soc. Trans. 1907, 1695).

The magnesium derivative of bromo-*p*-xylene condenses with chloral forming *βββ*-trichloro-*α*-xylyl ethyl alcohol, b.p. 158°/10 mm., which on prolonged boiling with potassium carbonate solution yields *xylylaldehyde* $C_6H_3Me_2{\cdot}CHO$ (Savariau, Compt. rend. 1908, 146, 297; Carré, *ibid.* 1909, 148, 1108). *o*-Xylyl bromide reacts with methyl aniline yielding *o*-xylylmethylaniline, b.p. 200°/35 mm., m.p. 34° (Von Braun, Ber. 1910, 43, 1353).

o-Xylylene bromide when treated with potash forms o-*xylylene oxide*  $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>O$, b.p. 192° (Willstätter and Veraguth, Ber. 1907, 40, 957). It also condenses with quinolines, aliphatic amines, and with *p*-amino-acetophenone (Scholtz and Wolfrum, *ibid.* 1910, 43, 2304).

The six possible tribromo xylenes have been obtained by Jaeger and Blanksma, by brominating the corresponding xylidines in glacial acetic acid and subjecting the dibromo xylidines so obtained to Sandmeyer's reaction; also by other methods (Proc. K. Akad. Wetensch, Amsterdam, 1905, 8, 153.

Recent literature on the xylyl and xylylene halogen derivatives: Radziewanowski and Schramm, Chem. Zentr. 1898, ii. 1019; Gabriel and Pinkus, Ber. 1893, 26, 2210; Klages and Knoevenagel, *ibid.* 1894, 27, 3024; *ibid.* 1896, 29, 310; Rupp, *ibid.* 1628; Curtius and Sprenger J. pr. Chem. [ii.] 62, 111; Halfpaap, Ber. 1903, 36, 1672; Noelting, *ibid.* 656; Fries, *ibid.* 1904, 37, 2338; Thiele and Balhorn, *ibid.* 1463; Willgerodt and Schmierer, *ibid.* 1905, 38, 1472; Dinesmann, Compt. rend. 1905, 141, 201; Stallard, Chem. Soc. Trans. 1906, 808; D. R. P. 230172.

Bromo- and *dibromo-*m*-xylylindigotin* are described in D. R. P. 154338, 1904.

Nitro derivatives. The nitration of *o*-xylene is fully described by Crossley and Renouf (Chem. Soc. Trans. 1909, 202); Crossley and Wren (*ibid.* 1911, 2341); Crossley and Morrell (*ibid.* 2345). The products obtained depend on the relative quantity of nitric acid used, on the temperature, the admixture of acetic or sulphuric acid, and on whether the nitric acid is added to the xylene or *vice versa* (*see* also Errera and Maltese, Gazz. chim. ital. 1903, 33, ii. 277; Konowaloff, J. Russ. Phys. Chem. Soc. 1905, 37, 530, 537).

Some recent literature: Morgan and Micklethwait, Chem. Soc. Trans. 1907, 360; Green, Davies and Horsfall, *ibid.* 2080; Errera and Maltese, Gazz. chim. ital. 1905, 35, ii. 370; *ibid.* 1909, 39, i. 517; Meisenheimer, Ber. 1906, 39, 2526; Blanksma, Rec. trav. chim. 1909, 28, 92; Chem. Weekblad, 1910, 7, 727).

Halogen nitro compounds are described by Crossley (Chem. Soc. Trans. 1904, 266); Konowaloff (J. Russ. Phys. Chem. Soc. 1904, 36, 537); Blanksma (Rec. trav. chim. 1906, 25, 373).

***p*-Xylylhydazine** $C_6H_3Me_2{\cdot}NH{\cdot}NH_2$ is formed by the reduction of sodium-*p*-xylenediazonium sulphite with zinc dust and acetic acid. The product is decomposed with hydrochloric acid and then treated with sodium hydroxide. It forms glistening, white slender needles, m.p. 78°, and yields many derivatives (Willgerodt and Lindenberg, J. pr. Chem. 1905, [ii.] 71, 398; Busch and Meussdörffer, *ibid.* 1907, [ii.] 75, 121; Plancher and Caravaggi, Atti. R. Accad. Lincei, 1905, [v.] 14, i. 157).

1 : 2 : 4-*Xylylhydrazine* forms yellowish-white needles, m.p. 57°.

Xylyl hydrazones and a number of their double compounds with aldehydes and their phototropy are discussed by Graziani (Atti. R. Accad. Lincei, 1910, [v.] 19, i. 489; *ibid.* ii. 193).

The reactions of *xylyl hydroxylamines* are described by Bamberger (Ber. 1902, 35, 3886; *ibid.* 1907, 40, 1893).

Xylyltriazine compounds have been prepared (Jovitschitsch, *ibid.* 1906, 39, 3821).

o-*Xylylene cyanide* condenses in presence of sodium ethoxide with *o*-diketones, keto acids, and esters of oxalic acid forming naphthalene derivatives (Hinsberg, Ber. 1910, 43, 1360; Wislicenus and Penndorf, *ibid.* 1837).

Xylene sulphonates are obtained by treating xylene with fuming sulphuric acid, and also by other methods (Jacobsen, *l.c.*; Wischin, Ber. 1890, 23, 3113; Pfannenstill, J. pr. Chem. 1892, [ii.] 46, 152, 154; Moody, Chem. Soc. Proc. 1891, 189; Junghahn, Chem. Zentr. 1903, i. 572; Maué, Annalen, 1903, 330, 46; Stallard, Chem. Soc. Trans. 1906, 808; Karslake and Bond, J. Amer. Chem. Soc. 1909, 31, 405).

Xylene sulphinic acids, -anhydride, and *-sulphoxide* are described by Smiles and Rossignol (Chem. Soc. Trans. 1908, 761); Hilditch (*ibid.* 1621); Knoevenagel and Polack (Ber. 1908, 41, 3323); Knoevenagel and Kenner (*ibid.* 3315).

p-*Xylylene hydrosulphide* is prepared by adding a boiling solution of *p*-xylylene bromide to alcoholic potassium hydrosulphide saturated with hydrogen sulphide. It is then separated from the glycol which forms at the same time.

by means of aqueous caustic soda. In the presence of hydrochloric acid it condenses with aliphatic aldehydes forming amorphous indefinite compounds, but with aromatic aldehydes it yields beautiful crystalline stable duplomercaptals containing an eighteen-membered ring. The *m*- and *o*- compounds yield similar derivatives (Autenrieth and Beuttel, Ber. 1909, 42, 4346, 4357).

Sulphides and *sulphones* have been prepared by Martynowicz (Chem. Zentr. 1910, ii. 1048), Strzelecka (*ibid.* 1135).

Xylyl ethers $(C_6H_4Me{\cdot}CH_2)_2O$ are described by Pawlowsky (J. Russ. Phys. Chem. Soc. 1911, 43, 214).

Xylene forms a large number of other derivatives, the following being some of the more recent literature on these: Blanksma, Rec. trav. chim. 1902, 21, 327; Stoermer and Atenstädt, Ber. 1902, 35, 3560; Scholl and Kačer, *ibid.* 1903, 36, 322; Kuhling and Falk, *ibid.* 1905, 38, 1215; Ullmann and Zlokasoff, *ibid.* 2111; Schmid and Decker, *ibid.* 1906, 39, 933; Bresler, Friedemann and Mai, *ibid.* 876; Jaweloff, *ibid.* 1195; Fecht, *ibid.* 1907, 40, 3890; Bamberger and others, *ibid.* 1932, 1949, 1956, 2258; Jacobson and Huber, *ibid.* 1908, 41, 660; Bülow and Schaub, *ibid.* 2355; Zeltner and Tarassoff, *ibid.* 1910, 43, 941; Braun, *ibid.* 1350; Morgan and Micklethwait, Chem. Soc. Trans. 1905, 1307; Clayton, *ibid.* 1906, 1054, 1295; Tröger and Hille, J. pr. Chem. 1905, [ii.] 71, 201, 236; Johnson, J. Amer. Chem. Soc. 1903, 25, 483; Andreasch and Zipser, Monatsh. 1905, 26, 1191; Haager and Doht, *ibid.* 1906, 27, 267; Barbier and Grignard, Compt. rend. 1909, 148, 646; Guyot and Esteva, *ibid.* 564; Layraud, Bull. Soc. chim. 1906, [iii.] 35, 223; Kozniewski and Marchlewski, Bull. Soc. Acad. Sci. Cracow, 1906, 81; Strzelecka, *ibid.* 1909, 731; Scholtz, Arch. Pharm. 1909, 247, 534; Fromm and Schneider, Annalen, 1906, 348, 161; Zincke, *ibid.* 1905, 339, 202; Gattermann, *ibid.* 1907, 357, 313; Auwers, *ibid.* 1909, 365, 291; Heinrich, *ibid.* 1910, 376, 139; Haller and Bauer, Compt. rend. 1911, 153, 21; Zincke and Breitwieser, Ber. 1911, 44, 176; Scholtz, *ibid.* 480; Diepolder, *ibid.* 2498; D. R. P. 234917; Halla, Monatsh. 1911, 32, 747; Buchner and Schulze, Annalen, 1910, 377, 259 (*v.* AZO-COLOURING MATTERS).

XYLENOL *v.* PHENOL AND ITS HOMOLOGUES.

XYLIDINES (*Aminoxylenes, Aminodimethylbenzenes*). Theory predicts the existence of six isomeric aminodimethylbenzenes, all of which are known. They are obtained by the reduction of the corresponding nitro compounds with tin and hydrochloric acid, or with iron filings and acetic acid, or, in the case of the commercial product, with iron turnings and hydrochloric acid.

1. *o*-3-**Xylidine**

$C_6H_3(CH_3)_2NH_2,(CH_3:CH_3:NH_2=1:2:3)$.

Liquid, boiling at 225° (corr.); sp.gr. 0·991 at 15°. Melting-point of the acetyl compound $C_6H_3(CH_3)_2NH(C_2H_3O)$, 131° (Töhl, Ber. 1885, 18, 2562; Jaeger and Blanksma, Rec. trav. chim. 1906, 25, 352).

2. *o*-4-**Xylidine**

$C_6H_3(CH_3)_2NH_2,(CH_3:CH_3:NH_2=1:2:4)$.

Lustrous rhomboidal tables, or large monoclinic crystals, melting at 50°; b.p. 226°; sp.gr. 1·0755 at 17·5°; m.p. of acetyl compound 99° (Limpach, Ber. 1888, 21, 646; Jaeger and Blanksma, *l.c.*).

3. *m*-2-**Xylidine**

$C_6H_3(CH_3)_2NH_2,(CH_3:NH_2:CH_3=1:2:3)$.

Liquid, boiling at 216° (corr.); m.p. of acetyl compound 177° (Grevingk, *ibid.* 1884, 17, 2430).

4. *m*-4-**Xylidine** or *as*-*m*-**xylidine**

$C_6H_3(CH_3)_2NH_2,(CH_3:CH_3:NH_2=1:3:4)$.

Liquid, boiling at 212°; sp.gr. 0·9184 at 15°; m.p. of acetyl compound 129° (Müller, *ibid.* 1887, 20, 1041; Limpach, *ibid.* 871; *ibid.* 1888, 21, 641; D. R. P. 34854).

5. *m*-5-**Xylidine** or *s*-*m*-**xylidine**

$C_6H_3(CH_3)_2NH_2,(CH_3:CH_3:NH_2=1:3:5)$.

Liquid, boiling at 220°–221° (corr.); sp.gr. 0·9935 at 0°; m.p. of acetyl compound 140·5° (Noyes, Amer. Chem. J. 20, 800; Töhl, Ber. 1885, 18, 362).

6. *p*-**Xylidine**

$C_6H_3(CH_3)_2NH_2,(CH_3:NH_2:CH_3=1:2:4)$.

Liquid, boiling at 215°; sp.gr. 0·980 at 15°; m.p. of acetyl compound 138°–139° (Witt, Noelting and Forel, Ber. 1885, 18, 2064; D. R. P. 34854; Frdl. i. 19).

According to Michael (Ber. 1893, 26, 39) *p*-xylidine, if chemically pure, crystallises when subjected to prolonged cooling, in large colourless tablets, m.p. 15·5°, b.p. 213·5°/762 mm. The acetyl derivative has m.p. 139·5°.

COMMERCIAL XYLIDINE.

The nitroxylene used in the manufacture of this product is prepared by the action of nitric acid on coal-tar xylene—a mixture of the three isomeric xylenes together with a small quantity of ethylbenzene (*v.* XYLENE). As *o*-xylene yields by direct nitration two mononitroxylenes, *m*-xylene two, and *p*-xylene one, it is evident that these five nitroxylenes will be contained in commercial nitroxylene, and, therefore, that the five corresponding xylidines will be present in the commercial xylidine obtained from it by reduction with iron turnings and hydrochloric acid. *m*-4-Xylidine is present in largest quantity; next to it, *p*-xylidine is the chief constituent, occurring to the extent of 20–25 p.c. Vaubel (J. Soc. Chem. Ind. 1897, 639) describes a method for estimating the various xylidines. If commercial xylidine is mixed with excess of concentrated hydrochloric acid, a magma of crystals separates, consisting mainly of the hydrochloride of *m*-4-xylidine (Schultz, Steinkohlentheer, 1, 339). *p*-Xylidine may be separated by the greater solubility of its sulphonic acid in dilute sulphuric acid, the base being afterwards regenerated by distilling the sodium salt of the sulphonic acid with dry ammonium chloride (Witt, Noelting, and Forel, J. Soc. Chem. Ind. 1889, 274; D. R. P. 139457). Commercial xylidine also contains amino-ethylbenzene (Noelting and Palmer, Ber. 1891, 24, 1957).

For the preparation of colouring matters, Limpach (Eng. Pat. 6899, May 9, 1888; J. Soc. Chem. Ind. 1889, 281) described the following method of separating the xylidines from the commercial product; 121 grms. of commercial xylidine are treated with 30 grms. of 100 p.c.

acetic acid, and allowed to stand for 24 hours. Crystals separate, which consist of pure *m*-4-xylidine acetate. The mother liquors are treated with hydrochloric acid, and after standing 3–4 days, about 20 p.c. of *p*-xylidine separates as hydrochloride.

A slightly modified form of this process has been described by Hodgkinson and Limpach (Chem. Soc. Trans. 1900, 65). The last filtrate which contains 2·7 p.c. of the *m*-2-xylidine and the two *o*- isomerides may be evaporated, and when the excess of acid and water is removed, on gently heating, the *m*-2-xylidine sublimes as the hydrochloride in beautiful silky needles. It may also be separated on a larger scale by conversion into the formyl derivative. The black residue, after the separation of the *m*-hydrochloride, is now dissolved in water and hydrolysed with sodium hydroxide. The product obtained on distilling alone or with steam is treated with formic acid, and the formyl derivatives of the two *o*-xylidines are separated by fractional crystallisation, the *o*-3-isomeride crystallising fairly readily, the *o*-4-isomeride only with difficulty. The *p*- and *m*- xylidines may also be separated by means of benzaldehyde, with which the *p*- isomeride yields di-*p*-amino-di-*p*-xylyl phenyl methane, m.p. 208° (Schultz, J. pr. Chem. 1907, [ii.] 76, 331).

Commercial xylidine is employed exclusively in the preparation of azo- colours, for which purpose it is either converted direct into diazoxylene, or first into amino-azo-xylene or into cumidine.

It should distil for the most part between the temperatures of 212° and 218°.

The xylidines form a large number of halogen, nitro-, sulphonic, and many other derivatives, many of which are used in the preparation of dyestuffs, thus:

m-4-Xylidine-5-sulphonic acid is obtained by heating *m*-4-xylidine (121 grms.) with con. sulphuric acid (106 grms.) *in vacuô* or in a current of air or indifferent gas for about 3 hours. It forms white, flat, quadratic rods or plates, is insoluble in common organic solvents and dissolves in water to the extent of 1 in 28·5 parts of water at 100°, and 1 in 250 at 0°. When diazotised it combines with β-naphthol, forming yellow and orange dyes for wool (Junghahn, Ber. 1902, 35, 3747).

Some of the more recent literature on the xylidines and their derivatives: Jablin-Gonnet, Bull. Soc. chim. 1891, [iii.] 6, 21; Menton, Annalen, 1891, 263, 361; Jacobson, *ibid.* 1895, 287, 211; Fries, *ibid.* 1906, 346, 128; Wallach. *ibid.* 1907, 353, 318; Heller, *ibid.* 1908, 358. 349; Lemoult, Compt. rend. 1904, 138, 815; *ibid.* 1906, 142, 1193; Simonet, *ibid.* 1905, 140, 788; Blanksma, Rec. trav. chim. 1905, 24, 46; Mannino and Donato, Gazz. chim. ital. 1908. 38, ii. 20; Fries, Ber. 1904, 37, 2338; Knoevenagel, *ibid.* 4073; *ibid.* 1909, 42, 3619; Diepolder. *ibid.* 2916; D. R. PP. 87615; 39947, 56322, 71969, 219210; Frdl. 1877–87, i. 9; 1890–94, iii. 20, 1001; 1894–97, iv. 66; Orton and King, Chem. Soc. Trans. 1911, 1188; Crossley and Morrell, *ibid.* 2345.

XYLIDINE PONCEAU *v.* Azo- colouring matters.

XYLIDINE RED *v.* Azo- colouring matters.

XYLIDINE SCARLET *v*, Azo- colouring matters.

XYLOHYDROQUINONE *v.* Phenol and its homologues.

XYLOÏDIN. A name applied by Braconnot to an explosive product $C_6H_8(NO_2)O_5$, obtained by the action of nitric acid on starch; and also to some varieties of collodion prepared by the action of nitric acid on wood-cellulose.

XYLONITE *v.* Celluloid.

XYLORCINOL *v.* Phenol and its homologues.

XYLORETIN *v.* Resins.

XYLOSE *v.* Carbohydrates.

Y

YEAST *v.* Fermentation.

YEASTS, FERMENTS OF, *v.* Fermentation.

YELLOW, ACID, *v.* Azo- colouring matters; also Naphthalene.

YELLOW, ANILINE, *v.* Azo- colouring matters.

YELLOW, BRILLIANT, *v.* Azo- colouring matters; also Naphthalene.

YELLOW, BUTTER, *v.* Azo- colouring matters.

YELLOW, CAMPOBELLO, *v.* Naphthalene.

YELLOW, CHROME, *v.* Chromium.

YELLOW, CITRON, *v.* Chromium.

YELLOW, COLOGNE *v.* Chromium.

YELLOW, CROCEÏN, *v.* Naphthalene.

YELLOW, FAST, *v.* Azo- colouring matters.

YELLOW, GOLDEN, *Martius yellow*, *v.* Naphthalene.

YELLOW, HESSIAN, *v.* Azo- colouring matters.

YELLOW, IMPERIAL, *v.* Aurantia.

YELLOW, KING'S, *v.* Arsenic; also Pigments.

YELLOW, LEIPSIC, *v.* Chromium.

YELLOW, LEMON, *v.* Chromium.

YELLOW, MANCHESTER, *v.* Naphthalene.

YELLOW, MARTIUS, *v.* Naphthalene.

YELLOW, METANIL, *v.* Azo- colouring matters.

YELLOW, NAPHTHALENE, *v.* Naphthalene.

YELLOW, NAPHTHOL, *v.* Naphthalene.

YELLOW, NEW, *v.* Naphthalene.

YELLOW, ORANGE, *v.* Azo- colouring matters.

YELLOW, PARIS. *Lead chromate* *v.* Chromium.

YELLOW, RESORCIN, *v.* Azo- colouring matters.

YELLOW, SALICYLIC, *v.* Salicylic acid.

YELLOW, SUN, *v.* AZO- COLOURING MATTERS; also STILBENE.

YELLOW, TURNER'S, *v.* PIGMENTS.

YELLOW ULTRAMARINE. *Citron yellow, Lemon yellow. Barium chromate*, *v.* CHROMIUM; also PIGMENTS.

YELLOW WOOD *v.* OLD FUSTIC.

YELLOW CEDAR. The *Rhodosphacra rhodanthema* [Engl.] or yellow cedar, a tree growing to the height of 70 or 80 ft., is indigenous to the northern part of New South Wales.

The colouring matter of this dyewood is *fisetin*, which is readily isolated by the method described in connection with YOUNG FUSTIC (Perkin, Chem. Soc. Trans. 1897, 71, 1194).

A second substance $C_{26}H_{30}O_{16}$?, colourless needles, m.p. 215°–217°, is also present in small amount, and may be identical with *fustin*, the glucoside of fisetin (Schmid, Ber. 1886, 19, 1755).

The shades given by the yellow cedar are slightly weaker and differ considerably from those given by young fustic (*Rhus Cotinus*), although both contain the same colouring matter. Employing mordanted woollen cloth, the following distinctions are observed—

	Chromium	*Aluminium*	*Tin*	*Iron*
Young fustic .	Reddish brown	Orange	Orange yellow	Brown olive
Yellow cedar .	Yellowish brown	Brownish yellow	Golden yellow	Olive

and these may be due to varying amounts of a brown extractive matter, which is contained in both plants. A. G. P.

YEW (*Taxus*; *If commun*, Fr.; *Eibe*, Ger.). It has long been known that the leaves and berries of the common yew, *Taxus baccata* (Linn.), (Bentl. and Trim. 253), possess powerful toxic properties. Yew is a reputed emmenagogue, and it has been used for the purpose of procuring criminal abortion, but its efficiency is more than doubtful, and its employment often leads to fatal consequences (*cf.* Redwood, Pharm. J. [iii.] 8, 361). The first thing to do in cases of poisoning is to empty the stomach; milk may then be given to allay irritation, and such stimulants as alcohol or ammonia employed. Yew is seldom used in medicine.

Chevallier and Lassaigne (J. Pharm. Chim. 1818, 4, 558), Peretti (*ibid.* 1828, 14, 537), Lucas (Arch. Pharm. [ii.] 85, 145), and others have examined yew chemically, but no definite compound was isolated till the discovery of an alkaloid *taxine* by Marmé in 1876 (Chem. Zentr. 1876, 166). Taxine was further studied by Amato and Capparelli (Gazz. chim. ital. 10, 349), who also obtained a non-nitrogenous crystalline compound *milossin*, and a *volatile oil* which distils with steam, and has the odour of fennel. The chemical reactions of taxine obtained by Marmé's process have been examined by Hilger and Brande (Ber. 23, 464). Taxine is prepared by exhausting yew leaves or seeds with alcohol or ether. The residue, after distilling off the alcohol or ether, is extracted with acidified water, and from the clear aqueous solution alkalis precipitate the base in white flakes, which, when washed and dried over sulphuric acid, assume the appearance of a white crystalline powder. The leaves contain more alkaloid than the seeds. The preliminary extractions of the leaves with alcohol or ether may be dispensed with; they can be treated directly with a weak solution of an acid. Thorpe and Stubbs (Chem. Soc. Trans. 81, 874) have investigated the conditions under which taxine can be extracted. They find that it undergoes change with extreme ease during the process of extraction, thus accounting for the difference in the description of its properties by earlier investigators. The method of extraction giving the best results was found to be treatment with dilute sulphuric acid (1 p.c.) in the cold. Taxine, so obtained, consists of very fine glistening particles or a white amorphous powder. It does not crystallise. It is odourless, but possesses a very bitter taste. It is very slightly soluble in water, is soluble in dilute acids, alcohol, ether, benzene, or chloroform, and insoluble in light petroleum. At 82° taxine practically melts, undergoing at the same time some decomposition. Analysis gives figures agreeing with the formula $C_{37}H_{52}O_{10}N$ proposed by Hilger and Brande. Taxine gives reactions characteristic of the alkaloids when treated with the usual reagents, and also combines with acids to form definite salts, which have, however, not been obtained crystalline. From the residue, insoluble in very dilute acids, after the removal of the taxine, alcohol and animal charcoal extracts milossin. Its purification is tedious and difficult. It crystallises in stellate groups of needles, which melt at 86°–87°, and which are insoluble in water, but soluble in boiling alcohol (Amato and Caparelli).

A glucoside, *taxicatin*, has been found in the leaves of the yew by Bourquelot (J. Pharm. Chim. [vi.] 23, 369). Taxicatin $C_{13}H_{22}O_7$, crystallises from alcohol in colourless needles, m.p. 169°–170° (corr.); the crystals obtained from aqueous solutions contain $2H_2O$. It is hydrolysed by emulsin or by 2 p.c. sulphuric acid into dextrose and a substance readily soluble in ether or chloroform (Lefebvre, *ibid.* [vi.] 26, 241).

The twigs of *Taxus baccata* were found to contain invertin and emulsin (Lefebvre), and raffinose and sucrose have been isolated from the leaves and twigs (Hérissey and Lefebvre, *ibid.* [vi.] 26, 56).

The amount of taxine present in the Irish yew, *Taxus baccata*, var. *Fastigiata* has been investigated by Moss (Sci. Proc. Roy. Dubl. Soc. 12, 92). The results seem to indicate that the Irish yew contains much more taxine than the common yew (*v.* VEGETO-ALKALOIDS). A. S.

YLANG-YLANG *v.* OILS, ESSENTIAL.

YOUNG FUSTIC consists of the wood of the stem and larger branches of the *Rhus Cotinus* (Linn.), a small tree which is a native of Southern Europe, and the West Indian Islands. It is a hard compact yellow wood, and is usually imported in small bundles or faggots. Within the last few years young fustic has almost disappeared from the market, not only on account of the artificial colouring matters, but because the shades it yields lack permanence, and the percentage of colouring matter it contains is small. The leaves of the *R. Cotinus* constitute *Venetian sumach*, a tanning material which is employed to some extent in Italy and Southern Europe.

Fisetin $C_{15}H_{10}O_6$. the colouring matter of young fustic was first isolated by Chevreul (Leçons de Chemie appliqués à la Teinture, A, ii. 150), who gave it the name '*Fustin*.' Bolley

(Schweiz. polyt. Zeitschr. 1864, 9, 22) considered that it was identical with quercetin, but Koch (Ber. 5, 285) maintained that fisetin was probably an aldehyde of quercetinic acid.

Schmid (Ber. 1886, 19, 1734), who carried out an exhaustive examination of this dyewood, obtained fisetin in a pure condition and proved that it was not identical with quercetin. He found that in addition to the free colouring matter, young fustic contains a glucoside of fisetin combined with tannic acid to which he gave the name of *fustin tannide*.

To prepare fisetin, Schmid (*l.c.*), and later Herzig (Monatsh. 12, 178) employed 'cotinin' (*v. infra*), a commercial preparation of young fustic which is no longer on the market. According to Perkin and Pate (Chem. Soc. Trans. 1895, 67, 648) fisetin is readily isolated from the dyewood as follows:—

Young fustic is extracted with boiling water, and the extract treated with lead acetate solution. The lead compound of the colouring matter is collected, made into a thin paste with water, and in a fine stream run into boiling dilute sulphuric acid. After removal of lead sulphate the dark-coloured filtrate, on cooling, deposits a semi-crystalline brownish mass, which is collected and purified by crystallisation from dilute alcohol.

Schmid assigned the formula $C_{23}H_{16}O_9$ to fisetin, but it was found by Herzig that the analyses agreed equally well with $C_{15}H_{10}O_6$, and that this formula was correct was supported by the work of Perkin and Pate (*l.c.*), who gave to fisetin sulphate the formula $C_{15}H_{10}O_6 \cdot H_2SO_4$.

Fisetin forms yellow needles, melting at above 360°, easily soluble in alcohol. Alkaline solutions dissolve it with a deep yellow colour which, on exposure to air, gradually changes to brown; with alcoholic ferric chloride it gives a deep green colouration, and with lead acetate a bright orange-red precipitate. *Tetra-acetyl fisetin* $C_{15}H_6O_6(C_2H_3O)_4$, m.p. 196°–198°, crystallises in colourless needles, and the *benzoyl* derivative $C_{15}H_6O_6(C_7H_5O)_4$ needles, melts at 180°–181° (P. and P.) (Schmid, 184°–185°). Fisetin gives with mineral acids in the presence of acetic acid crystalline salts. *Fisetin sulphate*

$$C_{15}H_{10}O_6 \cdot H_2SO_4,$$

scarlet needles, *fisetin hydrobromide*

$$C_{15}H_{10}O_6 \cdot HBr,$$

orange needles, and *fisetin hydrochloride* have been prepared in this manner (P. and P.). These compounds are readily decomposed by water. *Monopotassium fisetin* $C_{15}H_9O_6K$, yellow needles (Perkin, Chem. Soc. Trans. 1899, 75, 433) is obtained from fisetin by means of alcoholic potassium acetate.

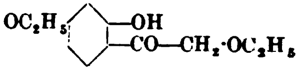
By fusion with alkali or by the oxidation of its alkaline solution by exposure to air fisetin gives *resorcinol* and *protocatechuic acid* (Herzig).

On ethylation with ethyl iodide fisetin is converted into *fisetin tetraethyl ether*

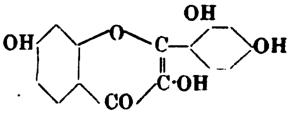
$$C_{15}H_6O_2(OC_2H_5)_4,$$

colourless needles, m.p. 106°–107°; the corresponding methyl derivative $C_{15}H_6O_2(OCH_3)_4$ melts at 152°–153°.

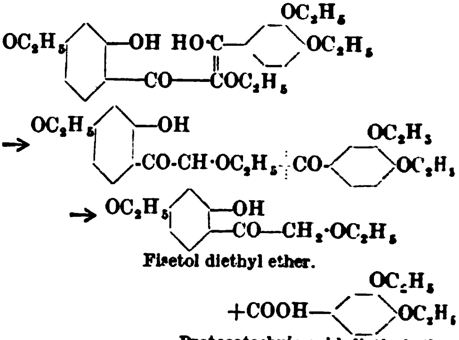
When fisetin tetraethyl ether is submitted to the action of boiling alcoholic potash it gives *protocatechuic acid diethyl ether*, and *fisetol diethyl ether* (Herzig), colourless needles, m.p. 42°–44°. This latter compound, by oxidation with permanganate, is converted into the *monoethyl ether* of *resorcylic acid*, and the *monoethyl ether* of *resorcinolglyoxylic acid*, and consequently fisetol diethyl ether may be thus represented



As a result of his investigation Herzig assigned to fisetin the constitution of a *trihydroxyflavonol*.



The tetraethyl derivative of this compound suffers hydrolysis according to the following scheme—

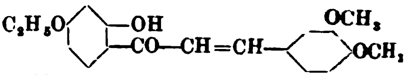


Fisetol diethyl ether.

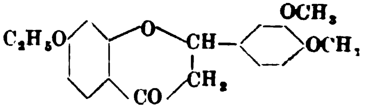
Protocatechuic acid diethyl ether.

Fisetin has been synthesised by v. Kostanecki, Lampe, and Tambor (Ber. 1904, 37, 784).

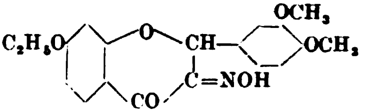
2′-Hydroxy-4′-ethoxy-3:4-dimethoxychalkone (I

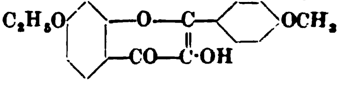
I. 

prepared by the condensation of resacetophenone-monoethyl ether with veratric aldehyde, when digested with boiling dilute alcoholic sulphuric acid gives 3-ethoxy-3′:4′-dimethoxyflavanone (II

II. 

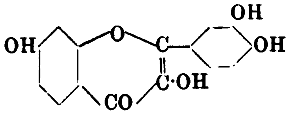
and this, when treated with amyl nitrite and strong hydrochloric acid in alcoholic solution, is converted into the *iso*nitroso compound (III)—

III. 

IV. 

When boiled in acetic acid solution with 10 p.c. sulphuric acid this substance gives 3-ethoxy-3′-4′-dimethoxyflavonol (IV). from which fisetin (V) is readily produced by the action of boiling hydriodic acid.

V.



Fisetin is a strong colouring matter and gives shades which are almost identical with those produced by quercetin, rhamnetin, and myricetin. The colours given with wool mordanted with chromium, aluminium, and tin are, respectively, red-brown, brown-orange, and bright red-orange (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1290).

The glucoside of fisetin, according to Schmid (*l.c.*), is prepared as follows: A boiling aqueous extract of young fustic is treated with lead acetate, the precipitate removed, the clear liquid freed from lead by means of sulphuretted hydrogen, and saturated with salt. The mixture is filtered, extracted with ethyl acetate, and the extract evaporated. There is thus obtained a residue consisting of the crude fustin-tannide, which is purified by solution in water, precipitation with salt, and extraction with ethyl acetate.

Fustin tannide crystallises in long yellowish-white needles, which are easily soluble in water, alcohol, and ether. When heated it decomposes above 200°. If a solution of fustin tannide in hot acetic acid is treated with water, and allowed to stand for some time, colourless crystals of *fustin* are gradually deposited.

Fustin crystallises from water in yellowish-white needles, m.p. 218°–219°, and when digested with boiling dilute sulphuric acid gives *fisetin* and a sugar, the nature of which has not been determined. The formula given to this glucoside $C_{55}H_{46}O_{23}$ by Schmid cannot be regarded as correct, in view of the fact that the true formula of fisetin is now known to be $C_{15}H_{10}O_6$.

Dyeing properties of young fustic. The colours derived from young fustic are all fugitive to light, hence this dyestuff has lost its importance. In silk dyeing it was formerly used for dyeing brown, the silk being mordanted with alum, and afterwards dyed with a decoction of young fustic, peachwood, and logwood. With the various metallic salts as mordants young fustic yields colours somewhat similar to those obtained from old fustic, the chromium colour is, however, much redder, being a reddish-brown, and the aluminium yellow is much duller; stannous chloride on the contrary gives an incomparably more brilliant orange, not unlike that obtainable from flavin or from Persian berries (Hummel). A. G. P.

YTTERBIUM (*Neoytterbium*). Sym. Yb. At.wt. 172·0. In 1878 Marignac, by the fractional decomposition of the nitrates, isolated from crude erbia the earth *ytterbia*, which has since been resolved by Urbain into two components *neoytterbia* and *lutecia* (Compt. rend. 1907, 145, 759; *cf.* Auer von Welsbach, Monatsh. 1906, 27, 935; 1908, 29, 181; Wenzel, Zeitsch. anorg. Chem. 1909, 64, 119; Urbain, Chem. Zeit. 1908, 32, 730).

Occurrence. Xenotime, ytterbite (gadolinite), monazite.

Separation and purification, v. LUTECIUM (*cf.* Urbain, Congress of Applied Chemistry, 1909, x. 94).

Ytterbium oxide (*Ytterbia*) Yb_2O_3, a colourless mass when free from thulia; it dissolves slowly in cold, and readily in hot, dilute acids. With the exception of scandia and lutecia, ytterbia (neoytterbia) is the weakest base of the yttrium earth series.

Ytterbium hydroxide $Yb(OH)_3$ is a colourless gelatinous precipitate.

Ytterbium chloride $YbCl_3,6H_2O$ (Matignon, Ann. Chim. Phys. 1906, [viii.] 8, 440), prepared by the action of hydrochloric acid on ytterbia, separates in deliquescent crystals, m.p. 150°–155°; it gives rise to the readily soluble **platinichloride** $2YbCl_3,PtCl_4,22H_2O$, and **aurichloride** $YbCl_3,AuCl_3,9H_2O$.

Ytterbium nitrate $Yb(NO_3)_3,4H_2O$ crystallises from strong nitric acid in transparent hygroscopic prisms; a trihydrate separating in colourless plates is obtained from solutions evaporated over strong sulphuric acid.

Ytterbium sulphate $Yb_2(SO_4)_3,8H_2O$, lustrous colourless crystals, the solubility of which diminishes with rise of temperature; this salt is partially hydrolysed in dilute solutions.

Ytterbium orthophosphate $YbPO_4,4\frac{1}{2}H_2O$, a gelatinous precipitate obtained from soluble ytterbium salts and sodium phosphate; the **metaphosphate** $Yb(PO_3)_3$, a crystalline powder, produced by melting together anhydrous ytterbium sulphate and metaphosphoric acid.

Ytterbium borate $YbBO_3$, obtained by fusing together ytterbia and boric anhydride, is a crystalline mass insoluble in dilute hydrochloric acid.

Ytterbium carbonate $Yb_2(CO_3)_3,4H_2O$, a gelatinous precipitate produced by mixing solutions of ytterbium nitrate and ammonium carbonate; the **basic carbonate** $Yb(OH)CO_3,H_2O$ is formed by passing carbon dioxide through freshly-precipitated ytterbium hydroxide.

Ytterbium oxalate $Yb_2(C_2O_4)_3,10H_2O$ is a crystalline powder distinctly more soluble in dilute sulphuric acid than the oxalates of yttrium and gadolinium (Nilson, Compt. rend 1879, 89, 419; 1880, 91, 56, 118). The normal ytterbium salts of the lower fatty acids are very soluble substances.

Spectra. Spark spectrum (i.) visible region (Thalén, *ibid.* 1880, 91, 326); (ii.) ultra-violet (v. Welsbach, Monatsh. 1884, 5, 1; Crookes, Proc. Roy. Soc. 1906, 78, A, 154). Arc spectrum (Exner and Haschek, Die Wellenlängen der Bogenspektra, 1904). G. T. M.

YTTRIUM. Sym. Y. At.wt. 89·0. Yttria, the predominant and most basic constituent of the yttrium earths, was first recognised by Mosander in 1843, and is the most easily purified oxide of this series.

Sources. The yttrium earths from the following minerals: ytterbite, xenotime, fergusonite, yttrotantalite, samarskite, polycrase, euxenite, yttrocrasite (Amer. J. Sci. 1906, [iv.] 22, 515). It also occurs in smaller quantities in the rare earths from cerite and allied minerals (*v.* CERIUM METALS AND EARTHS).

Separation and purification. In its basicity yttria follows the more basic cerite earths and is separated by methods founded on differences in basic strength from the other less basic yttrium earths, erbia, dysprosia, thulia, ytterbia, lutecia, and scandia, the following processes being employed for this purpose: (1) decomposition of nitrates; (2) the basic salt method (*v.* Lanthanum and Scandium); (3) fractional precipitation with alkalis or aniline; (4) successive treatment with ammonium carbonate and acetic acid.

Crystallisation methods are less practicable in the yttrium than in the cerium group, because of the greater solubility of the salts and the instability of the double nitrates, which in the yttrium series are unstable at the ordinary temperatures in aqueous or nitric acid solutions. Nevertheless, the final purification of yttrium from erbium, &c., may be effected by fractionation of the bromates, chromates, formates, acetates, oxalates, acetylacetonates, ethyl-sulphates, and ferrocyanides (*v.* Erbium).

Metallic yttrium has been obtained by the reduction of yttrium chloride or yttrium sodium chloride with sodium or by the electrolysis of the latter salt; it is an iron-grey substance easily oxidisable and decomposing hot water (Cleve, Bull. Soc. chim. 1873, [ii.] 18, 193, 289; 1874, [ii.] 21, 344; *cf.* Winkler, Ber. 1890, 23, 44, 120, 772, 2642).

Yttrium oxide (*Yttria*) Y_2O_3, white powder, sp.gr. 5·353, sp.ht. 0·1173, absorbing carbon dioxide from the atmosphere; obtained crystalline by fusion with calcium chloride (Compt. rend. 1888, 107, 99; J. Russ. Phys. Chem. Soc. 1910, 42, 96).

Yttrium hydroxide $Y(OH)_3$, gelatinous precipitate; the product obtained with ammonia in presence of hydrogen peroxide is a hydrated peroxide Y_4O_9,xH_2O (Cleve, Bull. Soc. chim. 1885, [ii.] 43, 53).

Yttrium carbide YC_2, yellow crystalline mass, sp.gr. 4·13, produced by heating the oxide with carbon in the electric furnace, is decomposed by water evolving acetylene, mixed with hydrogen, methane, and ethylene (Moissan and Étard, Compt. rend. 1896, 122, 573).

The salts of yttrium with colourless acid radicles are devoid of colour, and their solutions show no selective absorption in the visible region of the spectrum.

Yttrium fluoride $YF_3,\frac{1}{2}H_2O$ is obtained in the wet way as a gelatinous precipitate; the anhydrous substance is produced by the action of fluorine on the carbide (Moissan and Étard, *l.c.*).

Yttrium chloride YCl_3 can be produced by the methods generally applicable for the preparation of the anhydrous chlorides of the rare earths (*v.* Cerium). The hexahydrate

$$YCl_3,6H_2O,$$

colourless deliquescent prisms, melts at 160°, and is readily soluble in water or alcohol (Matignon, Ann. Chim. Phys. 1906, [viii.] 8, 433).

Yttrium sulphate $Y_2(SO_4)_3,8H_2O$, monoclinic crystals, isomorphous with the octahydrated sulphates of erbium, neodymium, and praseodymium (Kraus, Zeitsch. Krist. 1901, 34, 307). The **acid sulphate** $Y(SO_4H)_3$ separates from concentrated solutions in sulphuric acid (Brauner and Pičck. Zeitsch. anorg. Chem. 1904, 38, 322). With alkali sulphates, yttrium forms soluble double sulphates, *e.g.* $2Y_2(SO_4)_3,3K_2SO_4$;

$$Y_2(SO_4)_3,Na_2SO_4,2H_2O;$$

$Y_2(SO_4)_3,2(NH_4)_2SO_4,9H_2O$; these salts crystallise on concentrating the aqueous solution of their components.

Yttrium nitrate $Y(NO_3)_3,6H_2O$, very soluble deliquescent crystals; a dihydrate has also been described (Tanatar and Voljanski, J. Russ. Phys. Chem. Soc. 1910, 42, 586); basic nitrates, *e.g.* $3Y_2O_3,4N_2O_5.20H_2O$, are produced by the partial decomposition of the normal salt (James and Pratt, J. Amer. Chem. Soc. 1910, 32, 873).

Yttrium phosphates. The **ortho-phosphate** YPO_4, which occurs native as xenotime (*v. supra*), has been obtained in lustrous needles by melting together yttrium chloride and the amorphous phosphate (Compt. rend. 1875, 80, 304; 1888, 107, 622). When prepared in the wet way the crystalline salt has the composition $YPO_4,2H_2O$. The normal **pyro-** and **metaphosphates** $Y_4(P_2O_7)_3$ and $Y(PO_3)_3$ have been described together with several acid and double phosphates (Cleve, *l.c.*; Johnson, Ber. 1889, 22, 976).

Yttrium carbonate $Y_2(CO_3)_3,3H_2O$, white precipitate obtained either from a soluble yttrium salt and an alkali carbonate, or by passing carbon dioxide into freshly-precipitated yttrium hydroxide; it dissolves in excess of aqueous alkali carbonate forming double carbonates, *e.g.* $Y_2(CO_3)_3,Na_2CO_3,4H_2O$.

Yttrium oxalate $Y_2(C_2O_4)_3,9H_2O$, a white crystalline powder, dissolving in aqueous potassium oxalate to form $Y_2(C_2O_4)_3,3K_2C_2O_4,18H_2O$: it is soluble in dilute sulphuric acid to approximately the same extent as lanthanum oxalate.

Yttrium salts of other organic acids (*v.* Cleve, *l.c.*; Tanatar and Voljansky, *l.c.*; Benner, J. Amer. Chem. Soc. 1911, 33, 50).

Spectra. Spark spectrum; visible region (Thalén, Bull. Soc. chim. 1873, [ii.] 22, 350; Bunsen, Pogg. Ann. 1875, 155, 230, 366; v. Welsbach, Monatsh. 1884, 5, 1): ultra-violet region (Lohse, Ber. Berlin Akad. 1897, 179); Exner and Haschek, Ber. Wien. Akad. 1900, 109, II*a*, 122). Arc spectrum (Exner and Haschek, Die Wellenlängen der Bogenspektra, 1904; Eberhard, Zeitsch. wiss. Photograph. Photophysik. Photochem. 1909, 7, 245). Cathode luminescence (Crookes, Chem. Soc. Trans. 1889, 55, 255; Chem. News, 1889, 60, 27, 39, 51, 63; Muthmann and Baur, Ber. 1900, 33, 1748; Baur and Marc, *ibid.* 1901, 34, 2460).

G. T. M.

YTTROTANTALITE. A complex mineral consisting essentially of yttrium tantalate and crystallising in the orthorhombic system. It is black with a bright, conchoidal fracture, and closely resembles samarskite (*q.v.*) in appearance. Masses several pounds in weight have been found in the felspar quarries at Ytterby and Fahlun in Sweden and in the south of Norway (W. C. Brögger, Die Mineralien der südnorwegischen Granitpegmatitgänge, Vid.-Selsk. Skr. Kristiania, 1906, No. 6, 152). L. J. S.

Z

ZAFFRE. *Cobalt blue v.* Cobalt; also Pigments.

ZALA. A synonym for Borax.

ZANTHOXYLUM. The bark of the prickly ash, *Zanthoxylum americanum* (Mill.), and *Z. carolinianum*, which are rutaceous plants. Is used in medicine in the treatment of rheumatism and to relieve toothache. It contains a volatile oil and resin.

ZEÏN *v.* Maize, art. Cereals.

ZEIODELITE. The name of a mixture obtained by stirring 24 parts of finely-powdered glass into 20 parts of melted sulphur; used as a cement and for taking casts instead of sulphur or plaster.

ZEOLITES. A large group of minerals consisting of hydrated silicates of aluminium with alkalis and alkaline earths. A few of the more important are—

Natrolite (*q.v.*)	$Na_2Al_2Si_3O_{10},2H_2O$
Stilbite	$CaAl_2Si_6O_{16},6H_2O$
Heulandite	$CaAl_2Si_6O_{16},5H_2O$
Chabazite	$CaAl_2Si_4O_{12},6H_2O$
Analcite	$NaAlSi_2O_6,H_2O$
Thomsonite	$CaAl_2Si_2O_8,2\frac{1}{2}H_2O$

Harmotome and edingtonite contain barium; brewsterite contains some strontium; and potassium is present in phillipsite. These minerals hold their water of crystallisation very loosely, and it is replaceable by a variety of substances (*e.g.* ammonia, alcohol, &c.). They fuse readily with intumescence, hence the name zeolite, from ζεῖν, to boil, and λίθος, a stone. They are readily decomposed by acids, usually with the separation of gelatinous silica; and by the action of various reagents several substitution products have been prepared. They are minerals of secondary origin, occurring usually in the steam-cavities of volcanic rocks, and have been derived from the decomposition of felspar and other alkali-bearing minerals (with which they show certain chemical analogies).

The zeolites present many points of mineralogical interest, and they afford beautifully crystallised specimens, but they are of no direct economic importance. They appear, however, to play an important part in soils by retaining in a readily soluble form the alkalis set free on the weathering of felspar. The indefinite zeolitic constituent of soils has been named *geolyte* (Ger. *Bodenzeolith*) (E. A. Wülfing, Jahresh. Ver. Naturk. Württemberg, 1900, 66, 35; R. Gans, Zeolithe und ähnliche Verbindungen ihre Konstitution und Bedeutung für Technik und Landwirtschaft, Jahrb. K. Preuss. Geol. Landesanst, Berlin, for 1905, 1906, 179–211.)

On *permutite*, an artificial zeolite-like substance employed for softening water and for removing manganese and iron from water, and also used in sugar refining, *v.* R. Gans, Chem. Zentr. 1909, i. 2031; also art. Water.

L. J. S.

ZINC. Sym. Zn. At.wt. 64·88.

This metal was mentioned by Albertus Magnus, who died in 1280, the name then employed being 'golden marcasite.' The modern word zinc appears first in the writings of Paracelsus, about 1500.

The metal had, however, been produced at a much earlier date, probably by accident. Zinc bracelets were discovered in the ruins of Cameros, destroyed *circa* 500 B.C. Libavius carefully examined the properties of zinc about 1595.

Ores of zinc were known to the ancients, and were employed by them both for the manufacture of brass by the calamine process, and also in medicine. The working of zinc ores in Europe in modern times dates from the introduction of the use of brass, and there are records extant which show that in 1439 the Vieille Montagne calamine mines had been worked for a considerable time by the men of Aix. Metallic zinc was sometimes produced accidentally during the smelting of copper, but is stated to have been first made directly from calamine by Henckel in 1721 (Percy, Metallurgy, i. 520). A zinc factory was erected at Bristol by Champion in 1743; but the production in this country was small, the greater part of the metal required being imported from China and India, and zinc is stated to have sold in 1731 for £260 per ton, or more than ten times its present value. Other works were erected in the United Kingdom, and the demand gradually increased with the introduction of the direct method for the manufacture of brass. In England the process of distillation *per descensum* in fireclay crucibles was adopted; this has scarcely been used elsewhere, and is now completely abandoned in this country. The important zinc industry of Silesia in Germany was commenced in 1799 by Ruhberg, who had learned the process in England. The Liège (or Belgian) process was invented by Daniel Douy in 1809, and works were immediately erected for carrying out the process at Liège. These works ultimately developed into the Société de la Vieille Montagne in 1837, and this Société is now the largest zinc-producing company in the world. Zinc smelting was not introduced into the United States until 1850. It was not till 1820 that the exports of zinc from England to India about equalled the total imports, and this country could be considered for the first time to supply itself with zinc. Since that time, however, the trade has fluctuated considerably, so that in 1864 the total production of zinc in the United Kingdom did not equal one half of that required in the Birmingham brass trade alone.

In recent years the world's production of zinc (or 'spelter') has steadily increased, though the industry is limited to comparatively few centres. On the continent smelting is conducted in Belgium, Westphalia, and Silesia; in America the centres are Kansas, Illinois, and New Jersey; in the United Kingdom at Swansea and near Birmingham. The world's production of zinc in 1907 was 737,500 metric tons, the chief producers being—

United States . .	226,400 tons
Germany . . .	208,200 „
Belgium . . .	154,470 „
France and Spain .	55,730 „
United Kingdom . .	55,600 „

The greater part of the zinc smelted in the United Kingdom is now obtained from imported ores, the zinc ore raised in 1911 being only 17,652 tons. The Derbyshire mines were once of great importance, but their output now is negligible. Between 1880 and 1910 the British production of zinc increased tenfold. In addition about 100,000 tons of crude spelter are annually imported. At the end of the nineteenth century a very important zinc industry had grown up in Kansas. It depended largely on natural gas for fuel, and with the gradual exhaustion of the gas supply many spelter works were closed, and the industry migrated to the coalfields of Illinois or to Joplin.

Ores of zinc. The most important ores of zinc are the sulphide and carbonate. *Zinc blende* (ZnS) is commonly called 'black jack' by the miner on account of its dead black colour and high lustre. The use of blende for the manufacture of zinc and brass was patented in 1758 by Champion of Bristol. Previously the source of the metal was the carbonate, *calamine* ($ZnCO_3$), and this was the only ore used in Belgium until about 1855, when roasting of blende was adopted. Both these ores are widely distributed and are now extensively employed. Of less importance are the oxide (which usually contains oxide of manganese, and from its colour is called red oxide of zinc), and the silicates.

In New Jersey red oxide of zinc occurs together with magnetic oxide of iron in *Franklinite* from which the zinc is first extracted, and the residue is afterwards smelted for spiegel-eisen in the blast furnace. For ores which consist largely of oxide of zinc, but with some iron, magnetic concentration is now employed, the magnetite being removed, and an ore suitable for the zinc smelter obtained. The flue dust from the blast furnace used in the manufacture of iron is also frequently sufficiently rich in zinc to render its extraction advantageous.

Extraction of zinc. It is necessary that the ores used for the extraction of zinc should be as rich and as uniform in character as possible. The ore as purchased by the smelter usually contains at least 50 p.c. of zinc, though 45 or even 40 p.c. ores are used if they contain other valuable materials to replace the decrease in zinc. The ores as they occur are often only poor in zinc, and require to be concentrated by washing; in the case of calamine ores this is usually a simple matter, but with blendes which are frequently associated with other sulphides concentration is a more complicated operation, though with modern appliances, careful sizing, and the necessary attention, a remarkably perfect separation can be effected. The slimes produced during concentration are again treated, 'frue vanners' being now used for this purpose, and such portions as are rich in zinc are dried and smelted in mixture with other materials as afterwards described.

'Complex' ores, *i.e.* ores containing other metals in addition to zinc, have been the cause of considerable loss in times past, and enormous quantities of tailings were accumulated. These are now treated by flotation processes which separate the metallic sulphides from the gangue. In oil separation processes the dry, finely-crushed ore is mixed with a small quantity of oil, and is then washed with water. The metallic particles, or other bodies with smooth surfaces like sulphides, are wetted by the oil, and float upon the water, while the earthy portions sink to the bottom. In the Elmore oil vacuum process separation is assisted by the aid of partial exhaustion of a large metal receiver into which the oiled slimes and water enter. The air films surrounding the oiled particles are thus expanded and the separation much improved. In other cases diluted acid is employed, and with suitable ores gas bubbles are produced which cause the particles rich in metal to rise to the surface of the liquid. These flotation processes are now of such importance that from the Central mine at Broken Hill in Australia one-tenth of the total zinc ore of the world is obtained. The original ore contains 16·5 p.c. lead, 18·5 p.c. zinc, and 13 oz. of silver per ton. The concentrates account for 90 p.c. of the lead present, 85 p.c. of the zinc, and 88 p.c. of the silver (Sulman, Jour. Inst. Min. and Metallurgy, 1911, 47, 20).

When the ores have been thus concentrated, they are calcined or roasted to convert them as completely as possible into zinc oxide. Calamine is readily calcined, and this is frequently conducted in kilns with the waste heat from the smelting furnaces. On the other hand, blende requires much care and experience in roasting, so as to prevent the formation of difficultly decomposable sulphate. Blende is generally roasted in multiple-bedded reverberatory furnaces, sometimes with the waste heat from the smelting furnaces. By the use of multiple-bedded roasting furnaces a considerable economy of fuel and more uniform heating are obtained. It has generally been considered that the presence of any sulphur in roasted blende leads to loss of zinc, owing to sulphide being left in the retort, but, according to A. Voigt (J. Soc. Chem. Ind. 8, 986), the zinc left in the retort is chiefly in the form of oxide, while the sulphur in roasted blende is in the form of sulphates of metals generally other than zinc, and the presence of a small quantity of sulphur in roasted blende does not reduce the yield of zinc.

In roasting blendes a quantity of zinc fume is produced, and may lead to a somewhat considerable loss of zinc. This fume has been utilised by Krause-Cöthen for the manufacture of zinc carbonate (Berg. u. Hütt. Zeit. 1891, 246). The blende roasted at Oberhausen contains 0·02 p.c. of mercury. The dust deposited from the roasting kilns contains about 7 p.c. of mercury, which is extracted, and the sulphur dioxide from the gases is used for the manufacture of sulphuric acid (Chem. Zeit. 10, 1039).

Great advances have been made in recent years in the furnaces used for roasting blende, the object being to economise fuel and labour to obtain a more uniform product, and to utilise the sulphur dioxide evolved. This branch of the subject has been historically treated and fully illustrated by E. Schütz, Metallurgie, 1911, 635. One form of such furnace which has met with considerable favour is known as the Merton. It is multiple-bedded, and mechanically stirred.

After calcination the finely-divided ore is in all cases mixed with a suitable proportion of ground coal (non-caking), or other carbonaceous material, and heated to bright redness in a retort, the form and dimensions of which vary with the locality and the nature of the ore. The carbon unites with the oxygen of the ore to form carbon monoxide, and zinc is set free; the metal at the high temperature employed is converted into vapour, which is caused to pass into suitable receptacles, and condensed. The processes which are, or have been, used for the extraction of zinc differ merely in the form, arrangement, and number of the retorts, and in the methods adopted for supporting and heating them.

As the temperature at which the reaction $ZnO+C=Zn+CO$ takes place under ordinary atmospheric pressure is about 1050°, and nearly as high in a vacuum, the temperature of the retorts is necessarily high. The fuel consumption is therefore high, and the wear and tear of the retorts considerable. The difficulty of condensing the zinc vapour is increased by the fact that it is accompanied by carbon monoxide and other gases.

It is advantageous to thoroughly crush the materials, and to have as large a condensing space as possible. The condensers should be just sufficiently hot to keep the condensed metal in the liquid state, as, if the receivers are too hot, zinc is lost by volatilisation, while if the temperature is too low a coarse crystalline product is obtained. It is necessary that the retorts should be kept filled with carbon monoxide; if carbon dioxide is present, part of the zinc is oxidised and zinc and zinc oxide distil over together. For this reason it is necessary to leave a little of the ore unreduced in the retort at the end of the process (Steger, J. Soc. Chem. Ind. 5, 607).

The following general principles have been laid down for the construction of zinc furnaces by M. F. Laur (Bull. Soc. Indust. Minérale, 1874, 3, 395; Inst. C. E. 41, 317):—

1. That it is not prudent to construct furnaces the internal capacity of which exceeds about 32·5 cubic yards.

2. The thickness of the charge to be reduced in the muffles should not exceed 7 ins., and the vessels should not exceed 20 ins. in height, or 5 ft. in length.

3. The maximum capacity which can be advantageously given to the retorts is about 22 gallons.

4. The total internal volume of the retorts should be about one-third of the volume of the furnace in which they are heated, since experience shows that about two-thirds of the space is required for supports and free circulation.

Four processes for the extraction of zinc have been actually worked on a considerable scale—namely, the English, Carinthian, Belgian, and Silesian.

1. In the *English process*, adopted by Champion at Bristol, large fire-clay crucibles were used, and the method was that known as distillation *per descensum*. The process involved the use of an excessive amount of fuel, and only a comparatively small amount of zinc could be produced. This manufacture forms a very interesting chapter in the metallurgy of zinc, and has been fully treated by Dr. Percy (Metallurgy, i. 550), but as it has been entirely superseded, will not be here described in detail.

2. *The Carinthian process.* The process formerly adopted in Carinthia was in principle similar to the English method, the ore being charged into vertical pipes or retorts of fire-clay, and distillation being effected *per descensum*; a single furnace sometimes contained over 250 such pipes. This process is also now abandoned.

3 and 4. *Belgian and Silesian processes.* The only processes now in extensive operation for the smelting of zinc are the Belgian and Silesian, neither of which is confined to the countries in which it was invented. The two systems are sometimes combined in the same furnace, the retorts in the lower or hotter part being on the Silesian principle, and in the upper part on the Belgian. In each case the retorts are of fire-clay, and are generally made on the premises. In this country they are still frequently moulded by hand, then air-dried for about a fortnight, and afterwards heated to redness in a separate furnace before being set in position. By an improvement, the invention of M. Dor, which has been largely adopted on the Continent, and to some extent in the United Kingdom, the retorts are subjected to a pressure of 3000 lbs. to the square inch during manufacture. Great care is taken in the selection of suitable clays, in the preparation and tempering, and in pressing the retorts. They are thus made very thin, and yet possess great durability. The differences between the Belgian and Silesian systems are in the shape, size, and method of supporting the retorts, in the amount of charge used, and in the arrangement of the retorts in the furnace. In each system direct firing by coal was formerly universal and is still occasionally used, but gas-firing is now very generally employed. In Wales and in the United States regeneration by reversals, on the Siemens' principle, is generally adopted, but in Belgium continuous regeneration is preferred. In this system the gas producers are not separate from the furnace, but are placed in the furnace below the retorts. The products of combustion circulate by a zig-zag course through firebricks. The firebricks are provided with hollow channels, through which is drawn the air used for combustion. Such furnaces appear to work very satisfactorily and to require little attention or repair. The introduction of gas furnaces has led to considerable saving of fuel, which in Silesia was formerly 3·5 tons of coal per ton of ore, and is now about one-third of that quantity; gas firing has also led to the use of larger furnaces and given longer life to the retorts. The result has been that, in Silesia, while the number of works has actually decreased, the production of zinc has greatly increased (*v.* M. Georgi, Zinc Industry of Upper Silesia; Berg. u. Hütt. Zeitung, 36, 71, 78, 97; Inst. C. E. 49, 369).

The retorts used in the *Belgian process* are cylindrical or elliptical in shape, being closed at one end; these retorts are supported at the extremities, and are set in the furnace in tiers, each retort being inclined, and higher at the back than the front. The elliptical retorts are used for the lower tiers, where the temperature is highest, and they are sometimes air-cooled at the bottom. The introduction of the charge involves considerable skill. As the material is finely divided, particularly when fine concentrates are employed, it has been found advantageous to briquette the mixture by pressure, and this improvement is steadily gaining ground. The mouths of the retorts are fitted with condensing tubes of clay in which the zinc collects, partly in the form of metal and partly in the form of more or less oxidised dust, which deposits chiefly in a sheet-iron nozzle fitted to the clay tube. The workman judges of the progress of the operation by the colour of the flame or vapours which are evolved. Brown vapours are first given off, and with these any cadmium passes over; they are succeeded by the characteristic flame of zinc, which continues until the operation is completed. The loss of zinc by the Belgian process is about 10–15 p.c. of that originally present in the ore; while in the Silesian process, in which poorer and more refractory ores are employed, the loss is 5, or even 10, p.c. greater (F. Juretzka, Metallurgie, 1911, viii. 1).

In the *Silesian process* the retorts are ⌒ shaped; the width is the same as that of the Belgian retorts, but the height is greater, and as the retorts are supported in the furnace from beneath, they are made longer than in the Belgian process—consequently the charge is greater. The retorts are usually placed in a single row in the furnace, which occasionally contains as many as forty such retorts, though about thirty-two is stated to give the best results, and a smaller number is frequently employed. At Freiberg the muffles are arranged in two rows one above the other, and each row contains sixteen muffles. In recent years the tendency has been to use a much larger number of retorts than formerly, so that the charge of ore per furnace has been raised from 15 cwt. to 8 or 10 tons.

In the lower part of the front of a Silesian muffle a hole is provided for the purpose of introducing the charge, and removing the residue after the distillation is complete. This method of charging, combined with the underneath support, gives greater durability to the Silesian muffles, so that, though in a given time the Belgian furnace may make more zinc, the annual production is rather in favour of the Silesian (*v.* F. A. Thum. Notes on Zinc Smelting, Eng. and Min. Jour. 1879, 275; Inst. C. E. 58, 407). The cost of calcining the ore, and smelting the zinc, in a modern works in South Wales, averages about £3 per ton of spelter produced (1911).

The zinc works of Prince Hohenlohe in Silesia include three smelting works, with a total of 106 furnaces, and a separate calcining works for the preparation of zinc blende for distillation. The fourteen long double-bedded calcining furnaces employed have each an output of 220 lbs. of roasted ore every 5 hours. Each zinc furnace contains thirty-two muffles, heated by gas from Boetius producers. Every furnace is arranged with sixteen niches, each containing two muffles, while two furnaces are built together so as to form a double furnace. Two spaces are provided at either end of the double furnace, one for tempering the muffles, and the other for calcining the lump calamine. Most of the calamine is charged raw, as the carbon dioxide is driven off long before the temperature of reduction is reached. The charge per muffle weighs 507 lbs., and consists of a mixture of roasted blende, lump calamine, and dried slimes. The daily yield is about 108 lbs. of zinc. The zinc contains 3–4 p.c. of lead, which is reduced by refining to 1·07 p.c. The refining is conducted in a reverberatory furnace with an inclined base, in the well of which the metal collects, the lead at the bottom and the zinc above. Every 12 hours about half a ton of zinc is tapped, and the same amount of raw zinc is charged in; the lead is removed at longer intervals. An exactly similar process is used in Birmingham for refining Continental zinc previous to rolling. The refined zinc contains about 1 p.c. of lead, 0·02 p.c. of iron, and 0·04 p.c. of sulphur (Berg. und Hütt. J. 1889, 389; Inst. C. E. 101, 382).

For full particulars of modern practice in zinc smelting, especially in reference to the United States of America, W. R. Ingall's standard treatise on the Metallurgy of Zinc should be consulted.

The demand for spelter of high chemical purity is now considerable, such metal being required for the production of the ductile brasses. One of the most remarkable advances in connection with the metallurgy of zinc in recent years has been the improvement in the quality of the product when required for special purposes. Formerly 98 or 98·5 p.c. zinc was considered satisfactory, upwards of 1 p.c. of lead and a few tenths p.c. of iron being present. It is now possible to regularly obtain considerable quantities of metal guaranteed to contain over 99·75 p.c. of zinc, and upwards of 99·9 p.c. is also sold at a rather higher price. Such metal is either produced electrolytically, as afterwards mentioned, or by the use of a filter of carbon, firebrick, or other crushed and porous material placed in the mouth of the ordinary zinc retort. This filter retains the lead, while zinc vapour passes through and is condensed (*see* Primrose, Production of Pure Spelter, Inst. of Metals, 1909, ii. 231; Bannister, Carbonaceous Filters in the Smelting of Zinc, Inst. of Metals, 1910, i. 213).

Treatment of zinc ores in the blast furnace. In order to reduce the consumption of fuel and labour in the extraction of zinc a number of attempts have been made to reduce zinc in the blast furnace, but hitherto without much success. The difficulty experienced is due to the fact that the vapour of zinc and the furnace gases must, in such a furnace, pass away together, and during the condensation which ensues a reaction takes place between the zinc and the carbon dioxide of the gases, thus $Zn+CO_2=ZnO+CO$ reproducing oxide of zinc, and the ultimate result of the operation is merely to carry zinc oxide out of the blast furnace into the condensing apparatus. This action has been studied by Lencauchez (Mém. Soc. Ingén. Civils, 1877, 568; Inst. C. E. 51, 332), who found that zinc was still oxidised when the proportion of carbon dioxide was only 0·5 p.c. of the gas employed. Zinc vapour is also oxidised by any water vapour which may be present. By very rapid cooling of the gases Lencauchez succeeded in reducing the oxidation of the zinc to as little as 5 p.c., but after numerous experiments he concluded that this process is not likely to be commercially successful.

In some cases, with relatively poor complex ores containing zinc, a blast furnace smelting is adopted with the deliberate intention of volatilising the zinc as oxide. This is condensed, usually with the aid of bag filtration, and sold to the smelters to be dealt with in the ordinary way.

In 1878 Binon and Grandfils, in Stolberg, made the attempt to use a zinc oven with upright retorts. They aimed at making the old Carinthian method continuous. The materials containing zinc were heated with reducing agents by gas in reduction spaces in the form of shafts, which were filled above and emptied below.

Electric smelting of zinc. Considerable attention has been devoted to this subject during the past few years, and a lengthy list of patents has resulted. In the opinion of competent and disinterested observers the solution of the problem of the blast furnace reduction of zinc ores will come by means of the application of electricity. Two typical processes may be here mentioned. In that of Snyder, adopted in British Columbia, complex ores are calcined to oxides, mixed with fluxes to give a slag melting at about 1050°, and treated in an electric furnace. The current passes through the molten slag, under which the lead is collected in a well. The zinc is volatilised and condensed in suitable chambers. The De Laval process, worked in Sweden, is conducted in an arc furnace into which the roasted ores are charged after mixing with flux and coal. The product is a coarse metal containing zinc, lead, and other impurities. This coarse metal is refined by distillation in another furnace, and zinc of high purity is obtained, together with zinc dust or fume and base lead bullion. One h.p. year is claimed to produce 800–1000 k. of metallic zinc, much of which is, however, in the form of dust. The current cost is about half the total charges. The electric processes depend for their success upon electricity from cheap water power, and are not likely to seriously compete with the old-established reduction centres, at all events for some time to come (*see* Sulman, J. Inst. Min. and Met. 1911. lxi.; Min. Mag. 1911, 310, 389).

Wet methods of extracting zinc. One of the most difficult problems connected with the metallurgy of zinc is that of the treatment of complex ores. These may contain, in the aggregate, very considerable proportions of metallic constituents, but in that a number of metals are present together the ores cannot be treated by ordinary methods. Such ores usually contain about 12–28 p.c. of zinc, and 5–15 p.c. of lead, together with a few p.c. of copper, some ounces of silver per ton, and frequently small proportions of other constituents. Such ores are now frequently treated by oil vacuum or other concentration processes so as to classify the metalliferous portions into separate saleable products whenever possible. Various wet methods of extraction, usually connected with electro-deposition, have from time to time been suggested, and have been worked on a more or less considerable scale, though as yet usually without much commercial success. It was only after many trials that copper-refining by electro-deposition became a commercial success; and yet copper is worth more than double the price of zinc. The electro-motive force required for the deposition of copper is less than that necessary for zinc, and the strength of current that may be used with copper is greater. Thus electrolytic methods of extraction of zinc have to contend with the disadvantages of the comparatively low intrinsic value of the metal, and of comparatively slow deposition.

Where electro-deposition is employed, there are two methods open for extracting the zinc; in the first the ore itself may be used as anode; or, secondly, the ore may be roasted or treated with solvents to convert the zinc into a soluble form.

1. Luckow proposed to mix the ore with coke in order to render it a conductor, and to place it in an open chest in an electrolyte consisting of a somewhat strong and acid solution of common salt or zinc chloride (20–30 p.c. Zn). The metal was deposited either upon a zinc plate or upon a cathode of coke. Higgs (Eng. Pat. 9158, 1886) proposed a similar method, but used magnesium chloride as electrolyte, and adopted special arrangements for collecting the evolved chlorine.

2. Many processes have been proposed for rendering the zinc in complex ores soluble, and in a number of these it is proposed to recover the zinc from solution by electro-deposition.

Lambotte and Doucet proposed to roast blende to oxide, dissolve in crude hydrochloric acid, precipitate the iron with chloride of lime and zinc oxide, and electrolyse the solution.

Parnell calcined complex ores to oxide, dissolved in dilute sulphuric acid, which was obtained as a by-product, precipitated the copper by metallic iron, and evaporated the liquor to a mud. Zinc sulphide was then added, and zinc oxide produced by heating the mixture strongly. The zinc oxide so obtained was sold to the smelters. Maxwell Lyte calcined the ore, and dissolved in hot dilute hydrochloric acid; the lead was allowed to separate as chloride on cooling, the iron precipitated by limestone, the copper with scrap iron, and the zinc as oxide by lime. Létrange was one of the earliest workers in the direction of electro-deposition of zinc; in his process blende was carefully roasted at low temperatures to produce zinc sulphate, which was dissolved with hot water and dilute sulphuric acid. The solution was then electrolysed, using an anode of lead (or carbon) and a cathode of zinc. The current used must have a high electro-motive force owing to the peroxidation of the surface of the lead.

Among other suggestions the following are worthy of notice. In 1886 Lea and Hammond (Eng. Pat. 10868) suggested the use of hydrochloric acid as a solvent for roasted ores previous to electro-deposition, while in the same year Squire and Currie (Eng. Pats. 12249 and 12630) proposed the use of an alkaline solution for the same purpose, and in 1887 Watt patented (Eng. Pat. 6294) the application of dilute vegetable acids for a similar object. Again, Burghardt (Eng. Pats. 8986 and 13182, 1888; 659, 1889) proposed the use of an alkaline solution made by adding the roasted ore, previously mixed with 3–7 p.c. of powdered coal or charcoal, to melted caustic potash or soda. The mass was extracted with water, the zinc electro-deposited, and the alkali recovered to be used over again. Croselmire (Eng. Pat. 4286, 1888) proposed to mix the ground ore with clay, and form into perforated pressed bricks which are roasted into sulphate in kilns. The roasted mass is extracted with hot water and an equivalent of dilute sulphuric acid, air is blown through the liquors to precipitate iron and manganese, and, after settling, the clear liquor is electrolysed, or the zinc may be precipitated by soda ash. In

1889, also, Cunningham (Eng. Pat. 9987) again patented the use of an alkaline solution obtained by fusion with caustic soda.

Among methods of another class proposed for the treatment of complex zinc ores may be mentioned that of Perino (Eng. Pat. 10657, 1888) who fused the blende in clay retorts at 150°–200° with ferric nitrate in the proportion of about 5 parts of nitrate of iron to 1 of zinc. The mass was extracted with water and a solution of zinc sulphate obtained. Arrangements were made for recovering the ferric nitrate. Siemens and Halske also (Eng. Pat. 3533, 1889) use ferric sulphate for extracting zinc from complex ores, while Seegall (Eng. Pat. 4871, 1889) employs a slightly acidified solution of ferric chloride for the same purpose.

The complex ores of Leadville, U.S.A., containing 25 p.c. zinc, 15 p.c. lead, 20 p.c. iron, are roasted to sulphate, extracted with water; the residue chlorinised to complete the extraction of the zinc, and the zinc precipitated from the solutions as oxide (J. Soc. Chem. Ind. 7, 572).

The only process for the electrolytic production of zinc which is at present successfully conducted on a considerable scale in the United Kingdom is a modification of the Höpfner patent, introduced at Northwich by Messrs. Brunner, Mond, Ltd. The primary object is the production of chlorine from the calcium chloride liquors made in the ammonia-soda alkali process. These liquors are treated with zinc oxide (roasted zinc ores) and carbon dioxide, when calcium carbonate is produced and zinc chloride liquors obtained. This solution, after the removal of all the more electro-negative elements, is electrolysed, a current density of as much as 30 amperes per sq. ft. of cathode surface being allowable. The products are zinc and chlorine. The cathode consists of a series of discs of iron which revolve on a horizontal axis; the anodes are of carbon and are enclosed in wooden frames, the sides of which are enclosed with cloth diaphragms. The chlorine evolved is subsequently converted into bleaching powder. The zinc is stripped off the cathode plates, remelted, and cast into ingots. The great difficulty is to obtain a smooth adherent coating of zinc, and to prevent, as far as possible, the formation of spongy zinc. The exact nature of the latter product, and the cause of its formation, are still not thoroughly understood. This is doubtless the reason for the monopoly enjoyed by the above firm, the precise details of the process being kept secret. The zinc obtained is sold with a guaranteed purity of 99·96 p.c., which makes it of great value in the production of ductile brasses, and for other purposes where the presence of lead, &c. would be detrimental.

To avoid the necessity for electrolysis of the zinc solutions obtained from complex ores processes have been introduced to precipitate the zinc in a form suitable for sale to the zinc smelter. A typical process is that in which sulphur dioxide, obtained from blende roasting, is used to extract zinc from roasted ores. With excess of sulphur dioxide the zinc passes into solution as bisulphite, and is separated from the residues. These contain lead, silver, &c., and are sold to the smelters. By the removal of half the sulphur dioxide from the solution insoluble zinc sulphite is thrown down. This sulphite is filtered off, dried, and calcined in a muffle at a low temperature. Zinc oxide is obtained in a form suitable for spelter production, and the sulphur dioxide is added to the calciner gases to enrich them for fresh leaching operations (Eng. Pat. 21759, 1908).

Properties. Zinc is a bluish-white metal, which at ordinary temperatures is brittle, and when pure exhibits a beautifully crystalline fracture. The presence of impurities usually renders the fracture closer in the grain and less brilliant. Zinc melts at 420°, and boils at 930°. It can, however, be readily distilled in glass vessels in a vacuum, under atmospheric pressure. It undergoes two marked changes in electric conductivity, one at 170°, and the second at 340°. It is, therefore, believed by Benedicks to exist in these allotropic modifications (Metallurgie, 1910, 7, 531). Its tensile strength varies greatly according to the mode of preparation; cast zinc has a tenacity of only 1·2 tons per square inch, whilst an annealed rod gave a tenacity of 7·9 tons per square inch, and zinc wire 10 tons per square inch. Its hardness is intermediate between that of tin and copper, being equal to 6 on Turner's Sclerometer and 2½ on Moh's scale.

Though zinc is brittle at ordinary temperatures, and so tender above 200° that it can readily be crushed to powder, it can be rolled into sheet or drawn into wire at an intermediate temperature of about 100°–150°. It is a remarkable fact that the metal when so treated retains its malleability in the cold. Zinc was first rolled early in the present century in Birmingham, and rolled zinc now forms one of the most important applications of the metal, the greater part of the zinc produced in Europe being used for this purpose. Commercial zinc always contains more or less lead and iron, together with traces of cadmium, arsenic, and sulphur, the lead being volatilised with the zinc in the process of manufacture. Kosmann has also found comparatively large quantities of thallium in commercial zinc (Chem. Zeit. 10. 762). The chief technical methods for the assay of zinc have been described and discussed in connection with a paper by Greenwood and Brislee (Inst. of Metals, 1909, 2, 249). The presence of lead, which is objectionable in zinc to be used for the manufacture of the best qualities of strong brass, is an advantage in zinc that is to be rolled. As English zinc is relatively free from lead, it is usual to employ this variety for the production of alloys in which lead would be objectionable, while Continental zinc is imported for rolling. If the state of the market renders it advantageous to roll English zinc, this can be improved by the addition of a small proportion of lead. In addition to what is made here, more than 20,000 tons of sheet zinc is annually imported into the United Kingdom. The density of zinc varies from 6·8 to about 7·2 according to the mode of preparation.

When heated in the air much above its melting-point, zinc readily burns with a brilliant greenish-white flame, producing the oxide (ZnO) which condenses in a bulky flocculent condition formerly known as 'philosopher's wool.' The white fume produced when casting brass or other zinc alloys that melt at a tolerably high temperature consists of zinc oxide. Though zinc is readily volatile, the oxide is fixed at all ordinary furnace temperatures. Zinc is not affected by dry air at ordinary temperatures, but tarnishes superficially in moist air. The metal is also not attacked by mineral lubricating oils, and of ordinary animal oils it is attacked most by sperm oil and least by lard oil (Redwood, J. Soc. Chem. Ind. 5, 362). Zinc, both pure and commercial, dissolves readily in alkalis. Pure zinc is unattacked by water at boiling-point, and is almost unaffected by ordinary acids either diluted or strong. Commercial zinc, on the other hand, decomposes boiling water with the evolution of hydrogen, and is readily attacked by diluted sulphuric acid and by hydrochloric acid either diluted or strong. Impure zinc when amalgamated resists the action of acids exactly like pure zinc, and hence the zinc plates used in electric batteries are amalgamated so as to prevent the loss due to 'local action.'

This difference in the behaviour of pure and impure zinc towards acids has attracted much attention from chemists since the fact was first pointed out by A. de la Rive in 1830. Among the more important observations on the subject are those of Pullinger (Chem. Soc. Trans. 57, 815) and Weeren (Ber. 24, 1785).

Pullinger's conclusions are as follows:—Pure zinc with a perfectly smooth surface is not acted upon by dilute sulphuric acid that has been previously well boiled; pure zinc with a rough surface is readily acted upon, but less by acids that have been boiled than by those which have not. The presence of oxidising agents such as nitric acid, hydrogen peroxide, or electrolysed sulphuric acid, increases the rate of dissolution, while a reducing agent, such as hydriodic acid, almost entirely prevents dissolution; but reducing agents containing sulphur, such as sulphur dioxide, are without effect. It is not improbable that when zinc with a rough surface dissolves in dilute sulphuric acid the cause of dissolution is persulphuric acid, which acts catalytically, and in all probability *pure* dilute sulphuric acid would be without action upon metallic zinc, whether the surface of the latter be rough or smooth.

The solubility of impure zinc in diluted acids has been generally explained on the supposition that local electric currents are set up owing to the presence of the impurities, whilst with pure zinc no such currents are produced. Weeren, however, shows (*l.c.*) that the insolubility of pure zinc is due simply to the formation of a layer of condensed hydrogen on the surface of the metal, and thus the further action of the acid is stopped. Oxidising agents remove this film and assist dissolution; in impure zinc the hydrogen, obeying ordinary electrical laws, is evolved from the surface of the impurities. The fact that dissolution is much promoted by simply brushing the surface of the metal, or by allowing the action to take place in a vacuum, appears to afford strong support of this view, which is also quite in harmony with the fact that pure zinc dissolves much more rapidly in boiling dilute sulphuric acid, when the ebullition of the liquid removes any hydrogen from the surface of the metal, than at 98° where no ebullition occurs. Pure zinc with a rough surface, as Pullinger has shown, dissolves much more readily in diluted sulphuric acid than the same metal when the surface is perfectly smooth. Weeren suggests from the above facts that the difference in the action of diluted sulphuric acid on pure and impure zinc is capable of a simple mechanical explanation.

The question of the corrosion of zinc sheet and pipes, and of articles coated with zinc, when in use, is of great commercial importance. In dry pure air, as for instance in parts far removed from manufactories and towns, zinc roofing, when properly attached, lasts almost indefinitely with only a surface oxidation. But in the neighbourhood of towns, and especially in the vicinity of chemical manufactories, commercial zinc is rapidly corroded and spoiled. The presence of the slightest trace of free sulphuric or hydrochloric acid in the drainage water is very prejudicial. The presence of copper in any form in contact with zinc, should also be carefully avoided. Thus Müller has shown (Dingl. poly. J. 269, 280), that the zinc pipes which carried the drainage water from the copper dome of the royal castle at Brunswick, were rapidly attacked and corroded, while similar pipes on the opposite side of the same building were unaffected. The explanation of this difference probably was that in the presence of ammonia or of acids in the atmosphere some copper was dissolved by the rain water, and this copper being afterwards deposited on the surface of the zinc, set up an electric action resulting in the destruction of the pipes.

The use of galvanised iron tanks for water-cisterns has led to much controversy, particularly in the colonies, as to the effect of such storage on the health of persons who drink the water so stored. According to Bunte, the use of zinc-coated iron water-pipes is not deleterious to health, and this view is supported by Dr. Ehmann, late director of the water supply of Würtemburg, and by Dr. Boardman, of Boston (J. Soc. Chem. Ind. 6, 557). But a strong feeling exists to the contrary, and, after careful inquiry, the use of galvanised tanks for drinking-water was condemned in the British and French Navies. From the well-known properties of zinc it might be anticipated that some waters, which are either slightly acid or alkaline, would attack zinc vessels, while other waters might be almost without action. The presence of chlorides would probably also be prejudicial. It is not unlikely, therefore, that the differences in the action of water on zinc cisterns as noticed by various observers, is due in great measure to the character of the water. It is, however, certain that zinc or galvanised vessels should not be employed with acid waters.

Zinc-dust is employed somewhat largely as a reducing agent, as a precipitant for gold in the cyanide process for the extraction of gold from gold ores, and in the manufacture of fireworks. It is obtained, mixed with more or less oxide, in the distillation of the metal, or can be produced by crushing the metal in a mortar at a temperature somewhat below its melting-point.

In castings zinc takes a very sharp impression of the mould, and, as it melts at a low temperature, it has been used to a considerable extent, especially in France, for the production of statuettes and other objects of great beauty, which are afterwards usually coloured or bronzed. Some of these bronzes contain about 17 p.c. of copper; this alloy expands in the mould, and gives very sharp and clear impressions (*see* Turner and Murray, Inst. of Metals, 1909, ii. 115). The introduction of photo-engraving has also in recent years led to the use of considerable quantities of sheet zinc of special quality.

Galvanising. An important application of zinc, known as galvanising, was patented by Crawfurd in 1837. The object of the process is to coat the surface of iron with a thin layer of zinc, which protects the metal underneath from oxidation. In this respect zinc acts more perfectly than tin, which is negative to iron; in the case of tin plates the protection only lasts so long as the surface of the iron is covered with tin, but as soon as any portion of the iron is exposed to the action of the atmosphere oxidation proceeds more rapidly than in the absence of tin. Zinc, on the contrary, is more positive than iron, and thus, even though the coating of zinc may be removed in places, the protection continues so long as any zinc remains. Galvanised iron, however, cannot be used in contact with acids or alkalis, nor for the canning of fruits, meat, &c., on account of the action of vegetable acids and animal juices on the surface of the zinc.

The operation of galvanising is not in any way an electric process, as might be inferred from its name, but is simply a method of coating clean iron with zinc by immersion in a molten bath of the latter metal. Numerous patents have been obtained for suggested improvements in galvanising since Crawfurd introduced the process, particularly by Mallet and Morewood, but the old process is still almost universally adopted with a few improvements in details for saving of labour and the production of a better surface with a smaller consumption of zinc. Galvanising is conducted largely in the United Kingdom, and particularly in the neighbourhood of Birmingham and Wolverhampton, and in South Wales.

The iron or steel which is to be galvanised is received in the black state, coated with scale from the process of manufacture. Sheets are close annealed (*i.e.* annealed in large iron boxes, while carefully protected from access of air) to render them soft, but many other articles are treated without annealing. The scale is next removed by pickling in hydrochloric acid, which is used cold, or nearly cold, and which is contained in stone troughs. Tanks built of blue brick, set with sulphur joints, are also frequently used for containing the pickling acid. The strength of the acid depends on the character of the work; for wire 12 p.c. of real HCl is sufficient; for tubes, buckets, and general work an intermediate strength is best; while for sheets about 20 p.c. is generally used, and sometimes the undiluted muriatic acid of commerce (26–30 p.c.) is employed. By this method of working, pickling is usually complete in a few minutes; but on the Continent, where acid is dearer and economy is necessary, a dilute pickle is used, the water is heated, and the sheets are allowed to remain in the pickle for about 2 hours. The scale having been thus dissolved or loosened, the iron is washed with water, and, if necessary, rubbed with sand to complete the cleansing. The molten zinc is contained in a wrought-iron pot, the dimensions of which vary according to the character of the work to be done, and which is heated by means of a slow coke fire around the sides and under the bottom of the pot. The surface of the zinc is covered with powdered sal-ammoniac, which acts as a flux, and when best sheets are being treated it is usual to add about 2 or 3 p.c. of tin to the bath so as to assist in the production of a crystalline appearance of 'spangle' on the surface. In other cases re-melted zinc, *i.e.* zinc containing some tin and lead solder, is added to the bath for the same purpose. In galvanising sheets also it is usual to have a pair of rolls in the bath to guide the sheet in its passage through the zinc and to improve the surface. The consumption of zinc can be somewhat reduced, and the surface considerably improved, by the use of rolls or wire brushes as the sheet leaves the bath. Koffler and Breden (Eng. Pat. 12485, 1885; and 16674, 1888) have patented the use of wire brushes for this purpose; whilst Heathfield (Eng. Pat. 10089, 1886; and 1682, 1890) has introduced brushes which press evenly on the surface of the sheet as it leaves the bath, and he also adds fine wire brushes, together with improved rolls for feeding in the sheets. Corrugated sheets form a considerable portion of the trade; these are galvanised plain, and afterwards passed through corrugating machines in the cold. In galvanising wire, it is reeled through the pickle trough and the zinc-bath continuously, while netting is woven in the black, and afterwards reeled like wire. A continuous arrangement for this purpose has been patented by Vibart (Eng. Pat. 14297, 1889). The proportion of zinc taken up by the iron in galvanising varies considerably, being as high as 25 p.c. with moderately small wire, and less than one-fourth of this with many articles such as anchors, chains, and large elbows. In some galvanising works the sheets are pickled with hot diluted sulphuric acid, and the molten zinc is covered with zinc chloride instead of ammonium chloride; but the process above described is in much more general use.

The molten zinc gradually takes up iron during the galvanising process, and forms an alloy which is heavier than zinc, and which sinks to the bottom of the bath. This is removed from time to time and cast in plates, which, when broken, exhibit a close-grained fracture with black spots. This alloy is known as 'hard zinc,' and contains from about 2 to 5 p.c. of metallic iron. It is usually re-melted at a higher temperature, when it separates into two portions, one being tolerably pure zinc. The other portion is much less fusible, and forms a crystalline or granular material of the colour of zinc; it is very friable, and frequently exhibits surface colourations of great beauty. In this form it is generally sold to the smelter, and contains about 7·5 p.c. of iron, though exceptionally compounds are produced which contain upwards of 25 p.c. of iron.

The ammonium chloride used as a flux in galvanising is gradually lost during the process, and fresh additions have to be made as required. This loss is doubtless due in part to volatilisation of the salt itself, but also to a reaction which takes place, whereby zinc chloride is formed and ammonia set free. It has been proposed to collect the fume of ammonium compounds evolved from the galvanising bath by suitable exhausting arrangements and scrubbers in which the gases are washed by diluted acid, and it is stated that such an arrangement not only very much improves the atmosphere of the manufactory, but actually yields a profit in working.

The result of the action of the ammonium chloride and of atmospheric oxygen on the molten zinc during galvanising is the production of a scum which is known as 'flux skimmings,' and which is removed from time to time. This material consists of chloride and oxide of zinc, together with some ammonium chloride and dirt; it is usually sold to the smelters. Heathfield (Eng. Pat. 14411, 1885) proposed to dissolve the chlorides in water and deposit the zinc electrically: Richards (Eng. Pat. 13982, 1885) dissolves the oxide of zinc, together with the chlorides, in the minimum quantity of hydrochloric acid, and after evaporation electrolyses the concentrated solution of zinc chloride (*cf.* Ingalls, Metallurgy of Zinc, and ed. 578).

The electrolytic method has also been applied to the treatment of the zinc scum obtained during desilverising, and Rosing states (Dingl. poly. J. 263, 87) that this method is the most suitable for the purpose of any process at present known. The powdered scum is spread on a lead plate at the bottom of a wooden vat which is filled with a solution of zinc sulphate. The lead plate acts as anode, and when the current is passed, zinc deposits on the cathode, and a corresponding weight of zinc is dissolved from the scum. When the surface zinc has been thus removed, the residual mass is dried and heated to redness in a cupellation furnace and again electrolysed.

The quantity of hydrochloric acid annually used for pickling in the country is very great, as a number of firms engaged in the galvanising trade each require some thousands of tons of commercial muriatic acid (26–30 p.c.) per annum, but no statistics on this point are available. When the works are situated near the sea the waste pickle is readily disposed of, but the Midland manufacturers have during the last few years met with increasing difficulty in getting rid of their waste acid. The nuisance has become intolerable, and costly litigation has been undertaken by the local corporations to enforce some efficient system of treatment. Hitherto the usual system has been that of neutralisation with lime and subsequent filtration, with or without subsequent roasting of the ferrous precipitate, to convert it into red oxide of iron. Turner (Eng. Pat. 1889, 1890) introduced a method of recovering the hydrochloric acid, and the process has been in operation in South Staffordshire for over 20 years. The waste liquor, which consists of an acid solution of ferrous chloride, contains slightly under 10 p.c. of iron and about 15 p.c. of acid, chiefly in combination. The liquor is allowed to trickle slowly into a fire-brick reverberatory furnace of special construction; this is connected with condensers for the acid, which are arranged in the ordinary way. A bath of concentrated ferrous chloride solution is maintained in the furnace and thus prevents leakage, as the saturated solution penetrates any crack, and solidifies in coming in contact with the cool exterior of the furnace. The ferrous chloride is more strongly heated near the firebridge, and decomposes thus:—

$$2FeCl_2+2H_2O+O=4HCl+Fe_2O_3.$$

Hydrochloric acid is thus recovered and used over again, while the ferric oxide is raked out of the furnace and used as fettling in the puddling process. The fuel consumption is about 4 cwt. of gas coke per ton of waste liquor treated.

When sulphuric acid is used for pickling, the solution is evaporated and crystallised to produce copperas (commercial ferrous sulphate), for which there is a limited demand. In a few instances the copperas is afterwards decomposed by heat for the production of rouge, and other varieties of bright-red ferric oxide.

Dry galvanising. In the process known as 'sherardising,' introduced by S. Cowper-Coles, the articles which are to be coated with zinc are carefully cleaned and placed in closed boxes with zinc in a state of fine division. The boxes with their contents are then heated to a temperature insufficient to cause the zinc-dust to melt, and the vapour evolved gradually combines with the surface of the iron, and produces a closely adherent and protective coating of zinc. This process has been applied on a considerable scale, and is specially suited for articles which have sharp patterns upon their surfaces, or crevices which would be obliterated or filled up with zinc in the usual processes of dipping in molten zinc. The surface is somewhat less bright than usual, but is pleasing in appearance, and its wear is quite satisfactory.

Electro-galvanising. Iron or steel articles are now also frequently covered with zinc by deposition, with the electric current, from a neutral solution of zinc sulphate, or from zinc salts dissolved in caustic alkali. This process is not used for the general run of galvanising work, but more particularly for articles which are in a partly finished condition, or which are of such a special size or shape as to render the ordinary process unsuitable. Zinc coatings can thus be obtained which are quite satisfactory in wear and appearance, but they are apt at times to be soft and spongy, and not to adhere firmly to the surface of the iron. They are also more than usually subject to trouble from the development of black spots on the surface when exposed to moist air.

The nature of the zinc coating obtained by various processes has been studied in detail by Guertler, Metallographie, 1911, 353. The most complete account of the various processes of galvanizing is that given by M. A. Sing (Le Zingage du fer et de l'acier, Revue de Metallurgie, 1912, 1, 78, 160).

ALLOYS OF ZINC.

Zinc readily unites with most metals when the temperature is raised sufficiently to insure fusion. The *binary* alloys of zinc are generally white, crystalline, brittle materials, of limited importance. These alloys are usually of uniform composition; with lead and with bismuth, however, zinc unites at a temperature above its melting-point, but the alloys separate on cooling into two distinct layers, the upper layer in each case consisting of nearly pure zinc. The most important series of binary alloys of zinc is the copper-zinc (or brass) series, which is separately described.

With *aluminium* zinc readily unites when the metals are melted together in any proportions. The constitution of the series of alloys has been studied by Heycock and Neville (Chem. Soc. Trans. 1897, 389; Shepherd, J. Phys. Chem. 1905, 9, 504); Ewen and Turner (Jour. Inst. of Metals, 1910, 2, 140); and Rosenhain and Archbutt (Phil. Trans. A, 211, 315; also 10th Report Alloys Research, 1912). The phases which are recognised are α, which is zinc, or a solid solution containing less than 1 p.c. of aluminium; β, which is a definite compound, probably Al_2Zn_3; and γ, which is a solid solution of zinc in aluminium, and may contain as much as 40 p.c. of zinc. There is one eutectic, with 95 p.c. of zinc, melting at 380°, there is also a small break on the freezing-point curve at 85 p.c. of zinc, and an inversion at 256°, when the β-phase on cooling breaks up into α and γ. The commercially interesting alloys are at the aluminium end of the series, and these have assumed very considerable importance in recent years. The so-called aluminium castings used for motor cylinders and many similar purposes usually consist of about 10 p.c. of zinc; not unfrequently a few p.c. of copper or other metal or metals, and the residue aluminium. These alloys are rather more fusible than pure aluminium and are stronger and work better. They are also slightly cheaper. Alloys containing up to 25 p.c. of zinc can be rolled hot, at suitable temperatures, and material with tensile strength up to 34 tons per sq. in. obtained. The strength of these alloys is thus equal to that of mild steel, and as their density is only about 3–3·2 they have found considerable applications where lightness and strength are required. In sand cast alloys the maximum tensile strength is obtained with from 20 to 60 p.c. of aluminium, and the maximum hardness is within the same range. The tensile strength of all these alloys rapidly falls as the temperature rises. They are, therefore, not suitable for use when subjected to the effect of heat.

With *antimony*, zinc readily unites in all proportions; the resulting alloys are brittle, and exhibit a close-grained, dark-grey fracture when much antimony is present; when antimony is in excess, the surface of the alloys readily tarnishes during the process of casting, and the ingot becomes coated with a dark-grey crust of oxide. When the constituent metals are present in about equal proportions, surface colorations of great beauty can be obtained by oxidation, the tints obtainable including yellow, green, red, purple, and blue. A small proportion of antimony renders the surface colour of cast zinc distinctly more blue than usual, and with care the presence of 0·5 p.c. of antimony can be readily detected by this test. The usual colour of the surface of ingots, of equal parts of antimony and zinc, is a bright sky-blue, and the alloy has the peculiar property of marking glass (Turner). Antimony-zinc alloys are readily fusible, and in this respect the influence of antimony is quite different from that of arsenic or phosphorus, both of which raise the melting-point of zinc. Zinc-antimony alloys have met with an application for the production of thermopiles, for which purpose they are well suited.

With *bismuth*, zinc unites when the metals are melted together, but on cooling the alloy separates into two layers, the upper consisting of zinc containing bismuth, while the lower layer consists of bismuth containing zinc. The composition of the two layers varies with the temperature, the solubility of each metal in the other steadily increasing as the temperature rises until at about 850° the whole is of uniform composition (Heycock and Neville, Chem. Soc. Trans. 1897, 71, 390). With *gold*, zinc forms a series of alloys which are pale yellow, with excess of gold, and greenish as the proportion of zinc increases; all these alloys are more or less brittle. In the production of jewellery part of the copper used in the preparation of the gold alloys is often replaced by brass, as the colour of the resulting gold can be thus improved, while the cost of the alloy is slightly reduced. The presence of much zinc renders the gold hard and difficult to work, and as the zinc is volatile at high temperatures this alloy is not suitable for use where the article has to be reheated during manufacture. The compound AuZn, with 75·1 p.c. Au can be obtained by distilling off the excess of zinc from gold zinc alloys, in a vacuum, at 500° (Groves and Turner, Chem. Soc. Trans. 1912, 585).

With *iron*, zinc forms a series of alloys which are generally white, hard, and brittle. With not more than 5 p.c. of iron the alloys are close-grained and darker in colour than pure zinc; such alloys are produced in the process of galvanising, and are known as 'hard zinc.' With more iron the character of the alloy varies according to the method of preparation. The ferriferous residue left on liquating 'hard zinc' is very friable, and readily crushes into a coarse dust, consisting of bright flakes or spangles; on the other hand, the material obtained by fusion is compact, white, hard, and brittle. The alloy of zinc and iron obtained by saturating zinc near to its temperature of volatilisation with iron, is not attracted by a magnet; it does not rust, nor give sparks by friction or blows. It is dense in structure, but is only semi-metallic in fracture, and contains about 22 p.c. of iron. These alloys have a somewhat important application in the preparation of 'delta metal,' and also of Aich, sterro, and Gedge's metal, all of which are yellow brasses containing about 60 p.c. of copper and nearly 40 p.c. of zinc. The addition of iron to these brasses, first suggested by Keir in 1779, imparts special hardness, toughness, tenacity, and wearing properties, while the alloy can be rolled either hot or cold, and the constituents of the mixture are relatively cheap. The proportion of iron present usually varies from about ¼ to 4 p.c., according to the purpose for which the alloy is to be applied. The necessary zinc-iron alloy can be prepared by one of the following methods :—

1. By immersing clean iron wire, or sheet, in a bath of molten zinc heated to near its boiling-point. The addition of a little charcoal and some solid ammonium chloride assists the action. Where the presence of a little tin in the alloy is not objectionable (as for stere-metal) a convenient method is to employ clean tin-plate scrap; the coating of tin readily unites

with the zinc and leaves a clean surface of iron exposed to the action of the molten metal.

2. In order to reduce the waste of zinc usually accompanying the production of such alloys, a zinc of high boiling-point may be advantageously used in some cases. Bull (Eng. Pat. 4086, 1888) proposed the addition of phosphorus or arsenic for this purpose, while the addition of a little copper to the zinc assists the action without the introduction of any injurious constituent.

3. Alloys rich in iron can also be obtained by liquating the 'hard zinc' from galvanising works, and strongly heating the ferriferous residue in a closed crucible. The excess of zinc is volatilised, and the percentage of iron increases with the temperature employed. The alloys actually used in practice contain from about 7 to nearly 30 p.c. of metallic iron.

The equilibrium of the iron-zinc series has been studied by V. Vegesack (Zeitsch. anorg. Chem. 52, 1907, 30). The diagram is somewhat complicated. At the iron end there is a series of solid solutions in α, β, and γ iron with a maximum of about 35 p.c. of zinc at 1100°. At the zinc end two compounds are recognised $FeZn_7$ (or perhaps $FeZn_8$) and $FeZn_3$. These compounds undergo decomposition at 777° and 662° respectively. W. Guertler (Metallographie, 1911, 353) has recognised the compound $FeZn_8$ as an intermediate, electro-negative layer in the coating of galvanised iron, and occurring between the iron and the zinc coating. He has also recognised crystals of $FeZn_7$ in the external coating of zinc.

With *lead*, zinc readily combines when the two metals are melted together, but on cooling the mixture, or allowing it to remain at rest, the zinc collects as a layer at the upper surface, while the lead is found at the bottom of the mass. Neither of the metals is, however, quite pure, for the lead on cooling retains 1·6 p.c. of zinc, while the zinc retains 1·2 p.c. of lead (Percy, Metallurgy, 90). These proportions vary according to the method of treatment and the temperature employed. Thus E. Kraut has examined the behaviour of zinc containing lead on remelting (J. Soc. Chem. Ind. 5, 537). The sample was melted, well mixed, and a quantity removed and granulated. The residue was allowed to cool slowly, and the top, middle, and bottom of the mass separately analysed. The top contained 0·943 p.c. of lead, the middle 2·847 p.c., and a small quantity at the bottom as much as 4·121 p.c.; whilst the original zinc contained 1·543 p.c. of lead. In these experiments only 2 kilos. of metal was employed; on the large scale the separation of the two metals is still more complete.

The rolled zinc of commerce is a nearly saturated solution of lead in zinc, and usually contains about 1 p.c. of lead. An excess of lead injuriously affects the rolling properties: hence it is usual when rolling Continental zinc to remelt it in a reverberatory furnace with an inclined bed. The metal is allowed to remain fluid at a temperature a little above its melting-point, and the zinc is ladled off from the top from time to time. The excess of lead separates and collects as a layer in the lower end or 'sump' of the furnace, beneath the zinc, and is removed at suitable intervals.

On strongly heating lead-zinc alloys, the excess of zinc is at first volatilised, but as the temperature rises both lead and zinc distil over together. This curious volatility of lead in the presence of zinc is doubtless the cause of the occurrence of lead in commercial zinc, obtained from ores containing lead. The presence of a small proportion of zinc in commercial lead communicates hardness and allows the lead to receive a good polish without destroying its malleability.

With *mercury*, zinc readily unites to form a series of white brittle amalgams which become pasty when mercury is in excess. Zinc amalgams are easily obtained by mixing mercury with molten zinc, or by adding zinc to mercury heated nearly to its boiling-point. Zinc plates for galvanic batteries are coated with mercury by first cleaning the surface of the zinc with dilute sulphuric acid and then rubbing the mercury over the clean surface. An amalgam of zinc and tin is used on the rubbers of frictional electrical machines. On the literature of zinc-amalgams *v.* J. Soc. Chem. Ind. 9, 512.

With *silver*, zinc does not very rapidly unite at the melting-point of the latter, but at higher temperatures the metals readily combine, forming a series of alloys which are whiter than zinc, and the use of which has been proposed for coinage and other purposes. With 5, 10, or 20 p.c. of zinc, silver forms white ductile alloys, which can be rolled like standard silver, and which are more fusible than the corresponding copper alloys (Percy, Gold and Silver, 169–171).

When lead which contains silver or gold is melted with zinc and allowed to cool, the zinc separates, rises to the top, and solidifies first. This solid crust of zinc contains the precious metals, and this fact was applied by Parkes in the well-known process for desilverising argentiferous lead. The zinc scum is distilled to remove the zinc, much of which is recovered in the metallic state. The silver is melted, refined, and cast into ingots. The separation of the two metals is practically complete at 700° in a vacuum (Groves and Turner).

With *tin*, zinc readily unites in all proportions, the resulting alloys being generally harder than tin but softer than zinc. The colour of the alloys is in all cases white, and the fracture is crystalline, although its appearance varies with the mode of preparation. The alloys of tin and zinc are not quite uniform in composition, as the tin tends to separate and collect at the bottom on cooling. Tin-zinc alloys are used for castings of patterns for ornamental purposes. A detailed description of these alloys, based on the work of Guettier and Rudberg, is given in Hiorns' Mixed Metals, 249–253.

GERMAN SILVER, BRASS, &C.

In addition to the binary and other zinc alloys above mentioned, zinc enters into the composition of a number of alloys containing three or more metals, of which the following are the most important.

German silver (also known as Nickel Silver, Packfong, White Copper, Electrum, Nevada Silver, &c.) consists of copper, zinc, and nickel. It is an alloy of white, or nearly white colour, of high tenacity, and capable of being cast, rolled, spun, and otherwise worked. One of its most important properties is its relative permanence in the air, and this has led to the use of the alloy on a very extensive scale. It usually contains about 56–60 p.c. of copper, the proportions of zinc and nickel varying according to the price and use of the alloy; the zinc is seldom less than 14 or more than 30 p.c. of the whole. For castings a little lead is frequently added. Generally an alloy of about equal weights of zinc, and nickel is first prepared, and to this 'temper' the necessary quantities of copper and brass are added to give the required composition. A good description of the copper-nickel-zinc alloys will be found in Hiorns' Mixed Metals, 235–248.

One of the chief applications of German silver is in the electro-plate trade, for the production of articles of which teapots, forks, and spoons may be taken as examples. The alloys are melted in crucibles, deoxidised usually with manganese, cast into strips in metal moulds, and rolled, with several annealings, to the required gauge. For the production of ductile alloys pure metals must be used, and the temperature and character of the annealings carefully regulated. The character of the silver deposit in such articles has been studied by McWilliam and Barclay (Inst. of Metals, 1911, 1, 212), who conclude that when the proportion of nickel exceeds 14 p.c. the silver is more liable to strip off irregularly in actual use. With more nickel the strength and hardness increase and the alloy more nearly resembles silver in colour. Alloys containing 19–22 p.c. of nickel are specified for best work, and by suitable methods adherent coatings of silver, of excellent quality can be obtained (*ibid.* 226).

Part of the tin in *gun metal* and in *bearing metal* is frequently replaced by zinc, as it is found that the density and wearing properties of the alloy are thereby increased (*v. Bronze*, art. TIN). For the same reason the bronze coinage of this country contains 1 p.c. of zinc. Zinc is also present in some varieties of aluminium bronze and phosphor bronze in manganese bronze, and other similar alloys. The 'Biddery Ware' manufactured in India usually contains about 90 p.c. of zinc together with copper, lead, and tin in different proportions.

Copper alloys—Brass. *History.* Although the word brass frequently occurs in the Old Testament, there is little evidence that an alloy of zinc and copper was known in early times, unless, indeed, the suggestion be accepted that brass was sometimes accidentally produced in the manufacture of copper. The word translated 'brass' might equally well be rendered copper or bronze, both of which were in common use for a considerable period before the introduction of copper-zinc alloys (*v. Bronze*, art. TIN).

There is abundant evidence, however, that brass was known to the Romans about the beginning of the Christian era; that it was used for coinage purposes, and that it formed one of the yellow alloys known as *orichalcum*. The analytical and historical evidence on these points has been summarised by Dr. Percy (Metallurgy, i. 518–528; *cf.* Gowland, Presidential Address, Inst. of Metals, 1912). In the middle ages the Germans were famous for the production of brass, which was imported into this country chiefly in the form of sheet or *latten*, which was employed for the 'brasses' of churches, particularly in the Eastern counties. Over 4000 such brasses are known to exist in various churches &c. in the United Kingdom, which is far richer in this respect than any other country. The first brass manufactory in England is stated to have been erected by a German in Surrey about the middle of the seventeenth century. Brass works were started in Bristol in 1702; whilst the first works for making brass in Birmingham (now the centre of the brass trade) were erected about 1740 by Turner. Up till the middle of last century the only method used in the production of brass was the calamine, or cementation, process, in which copper, in the form of bean shot or sheet, was heated in crucibles in contact with calamine and carbon, with the result that zinc was liberated and volatilised, being afterwards absorbed by the copper. The brass thus produced was then melted down and cast. This process was slow and laborious, and only yielded a brass tolerably rich in copper. In 1781 James Emerson patented the direct production of brass from copper and zinc, although there is evidence that the method had been previously used to a limited extent. The calamine process was gradually superseded by the direct method of production, so that the last calamine brass works in this country were closed about 1850. Some of the most important factors in the development of the brass trade have been the introduction of rolling mills in the early part of last century, with the subsequent application of powerful machinery; the application of the stamp and die in 1769, whereby articles were produced more rapidly, with better finish, and with less metal than by the old process of casting; the introduction of gas fittings in the early part of the nineteenth century; the use of brass and copper tubes in locomotives and marine engines; the introduction of yellow metal sheathing; and the extended use of engineers' brass work and steam and water fittings, and lastly the applications to electric fittings. These and many other circumstances have resulted in an enormous development of the brass trade, so that there are employed in the brass trade of Birmingham alone over 35,000 persons (male and female), while the consumption of metal is valued at 4 millions sterling (v. A Short History of the Brass Trade, J. W. Davis; also Encyc. Brit. art. Brasses; Thomson, Hist. of Chemistry i. 55, 62, &c.; Midland Hardware District. 226–240; Percy, Metallurgy, 504; Holzapffel's Mechanical Manipulations, 312; Useful Metals and their Alloys, 566).

General properties of zinc-copper alloys. Zinc and copper unite in all proportions, the resulting alloys being of remarkably uniform composition throughout the mass (Laurie, Chem. Soc. Trans. 53, 106; 55, 677). The experiments of Tilden (J. Soc. Chem. Ind. 9, 84) also show the great uniformity in composition of commercial sheet brass, although on the other hand Hiorns (Mixed Metals, 107) gives analyses showing the copper to be less at the top than at the bottom of ingots of cast brass. The alloys containing upwards of 80 p.c. of copper are red or red-yellow in colour; those containing less than 48 p.c. of copper are grey or white; the intermediate alloys are yellow. The hardness of the alloys is usually greater, while the melting-point is higher, than that calculated from the mean of the constituents. The addition of zinc to copper produces remarkable alterations in the working properties of the product, varying, however, with the proportion of zinc present. Thus, pure copper can be rolled hot or cold, although in the latter case frequent annealing is necessary, and rolling hot is much cheaper and more expeditious. The addition of only a trace of zinc renders copper 'red short,' although it does not interfere with the malleability of the metal when cold. Hence alloys which contain from about 62 to 100 parts of copper p.c., and the residue zinc, cannot be rolled hot, or if so rolled require special treatment. Usually these alloys are rolled cold, and are annealed and pickled from time to time as the metal becomes hard and brittle from the work put upon it. But alloys with about 60 p.c. of copper can be rolled either hot or cold, and the cost of production is thus reduced. These alloys are, however, less ductile and tough than those which contain more copper. Their tensile strength is greater, but their ductility less than with alloys higher in the series. The alloy of 60 parts of copper and 40 of zinc was patented by Muntz for the production of sheathing for wooden ships, and is now largely prepared under the name of 'yellow metal,' for the production of the cheaper varieties of brass sheet, tubes, and wire. The standard size of yellow metal sheets is 14 by 48 ins., and the thickness is returned according to the Birmingham metal gauge. Alloys containing about 50 p.c. of copper are light yellow in colour; but cannot be rolled either hot or cold. The chief application of alloys containing rather more than half their weight of copper is for the production of 'brazing' solder for use with copper, brass, &c. These alloys form what is usually known as 'hard' solder, in contradistinction to lead-tin alloys or 'soft' solder. But in the brass trade different varieties of solder are used, containing from about 45 to 56 p.c. of copper, according to the temperature to be employed. The brazing solders containing more copper are called 'hard,' and those with more zinc 'soft.' The solder most commonly employed contains about 51 p.c. of copper, and is usually sold in the form of powder, which is prepared by heating a mass of the alloy to a particular temperature below its melting-point, when it is struck a sharp blow with a mallet. At this temperature the alloy is very friable, and readily crumbles into powder when treated as above described. If it is too hot or too cold it cannot be powdered in this way.

With more than 50 p.c. of zinc the alloys lose their yellow colour and become white, brittle, and more fusible. Though all these white alloys are brittle when hot or when cold, they can usually be laminated at some intermediate temperature, and in this respect they resemble zinc. This proper temperature varies according to the proportion of copper present, being as low as 150° in zinc, and at a red heat, probably about 600°, in yellow metal. As the copper increases beyond 60 p.c., as before explained, brass can no longer be rolled hot, but is laminated in the cold with repeated annealing.

According to Mallet (Construction of Artillery, 82), the alloy $CuZn_2$, containing about 33 p.c. copper and 67 p.c. zinc, is used for watchmaker's brass, and possesses the greatest tenacity of the whole series. This statement has been copied into many well-known works on the subject, but it is evidently an error. Laurie has shown by his investigations on the electro-motive force of zinc-copper alloys (*see* above) that only one definite alloy exists in this series. This compound is white, hard, and brittle, and corresponds very closely in composition to Mallet's alloy above mentioned. All other zinc-copper alloys may be considered as solidified solutions of this definite compound in excess of one or other of the constituent metals. Guertler (Zeitsch. anorg. Chem. 1906, 51, 397; 1907, 54, 58) and Murray and Turner (J. Inst. of Metals, 1909, 2, 131) support the view of only one definite compound in the copper-zinc series, viz. Cu_2Zn_3 with 39·36 p.c. Cu. This compound is a brilliant white brittle substance, harder than mild steel. Of itself it is of little or no practical value, but by its union with various proportions of copper, which alone is too soft, a whole series of alloys is obtained which possess most valuable and wonderfully graduated properties.

The equilibrium of the copper-zinc series has been studied by Roberts-Austen (4th Report Alloys Research); Shepherd (J. Phys. Chem. 1904, 8, 421), Tafel (Metallurgie, 5, 13), Hudson (J. Soc. Chem. Ind. 1906, 503), Murray and Turner (J. Inst. of Metals, 1909, 2, 103), and Carpenter and Edwards (*ibid.* 1911, 5, 127). The latest form of the equilibrium diagram of this series has been given and discussed by Rosenhain in the article on METALLOGRAPHY, and will, therefore, only receive brief reference here. The alloys, which are of commercial importance, contain from about 45 to 100 p.c. of copper. Within this range there are three constituents which are respectively designated by the Greek letters α, β, and γ. The α constituent is a solid solution of zinc in copper, the maximum content of zinc being about 36 p.c. at 400°. The γ constituent was regarded by Shepherd as a solid solution, but by Murray and Turner as the compound Cu_2Zn_3, containing about 40 p.c. copper. The β constituent contains about 52 p.c. copper. It has the properties of a solid solution, but is believed by Carpenter (J. Inst. of Metals, 1912) to be an intimate mixture of α and γ below a critical temperature of 470°. This critical temperature is noted with alloys containing from 60 p.c. of zinc down to 28 p.c., and probably less. The α phase is relatively soft and ductile: the β phase is harder and more brittle, while the γ phase is still harder, and practically has no ductility. It can be readily powdered in a mortar. The effect of adding zinc to copper is, therefore, as shown by Charpy, to increase the tenacity and to diminish the ductility. Beyond 40 p.c. the tenacity very rapidly falls away again, whilst the ductility is diminished after 30 p.c. Hence where ductility and strength are required together, as with cold-drawn tubes, or cartridge cases, about 70 p.c. copper is preferred. The chief commercial alloys may be classed as follows (Hudson):—

1. 100–71 p.c. Cu. Consist entirely of α at all temperatures.

2. 71–64 p.c. Cu. Entirely α below 400°; $\alpha+\beta$ above.
3. 64–63 p.c. Cu. Consist of $\alpha+\beta$ at all temperatures.
4. 63–53·5 p.c. Cu. $\alpha+\beta$ at low temperatures; β only at some higher temperature.
5. 53·5–51 p.c. Cu. Consist of β entirely at all temperatures.
6. 51–40 p.c. Cu. $\beta+\gamma$ at low temperatures; β only at a higher temperature.

It will be noted that the proportion of the β constituent increases as the temperature rises, and this fact has important bearings on the heat treatment of brass.

Cast brass. All brass is now made by melting together copper and zinc, but the term 'cast brass' is applied when the article to be made receives its form in the mould, and does not require to be afterwards rolled, drawn, hammered, or spun. For this purpose the charge is melted in graphite or clay crucibles, which usually contain about 90 lbs. of metal, and which are heated in small wind furnaces by coke. Generally each furnace contains but one pot, but sometimes two or four pots are placed in a single furnace, which is made proportionately larger in such cases. In Birmingham clay crucibles were formerly used for brass, and plumbago for bronze castings. Larger crucibles, holding 250 lbs. of metal, are often used in big foundries. Small cranes are then provided. In practice it is necessary to add a quantity of scrap brass to the charge, and this is generally introduced first into the red-hot crucible together with a small quantity of flux, which is added to remove the oxide and dirt adhering to the scrap. When only new metal is used the flux is either much reduced or altogether omitted. The fluxes most commonly employed are ground fluor spar, together with more or less glass, and *sal enixum* or acid potassium sulphate. When the scrap is hot the copper is charged into the crucible, usually in the form of ingots, though occasionally bean shot copper is used. After the copper has thoroughly melted, the zinc is cautiously added in as large pieces as possible. The use of large pieces of zinc reduces the loss, and moderates the violence of the combination. In any case considerable heat is produced by the union of zinc and copper, and some of the zinc burns with a dazzling brilliancy. After allowing the crucible to remain in the furnace a short time to permit the metal to become sufficiently fluid, it is poured into moulds, which for cast brass are generally of 'green' sand. While the brass is hot, zinc gradually volatilises and burns at the mouth of the crucible, forming zinc oxide; this produces the white fume which fills the casting house while the metal is being poured, and as a protection against the deleterious effects of inhaling the fume it is customary for the workman to keep his mouth and nostrils covered with a cloth. Regulations are now in force to ensure the proper ventilation of brass foundries. When the metal has set, the castings are turned out and dipped while warm into water, which detaches most of the adhering sand; the processes of dressing, grinding, polishing, dipping, and burnishing are necessary to give the required surface, while the finished article is lacquered to preserve it against atmospheric influences. The proportion of copper in cast brass varies considerably according to the purpose for which it is required; in some cases cheapness is of prime importance, in others the metal must 'dip' well when immersed in acid, while not unfrequently the shade of colour of the resulting alloy is of the utmost moment. Best cast brass generally contains from 70 to 75 p.c. of copper; ordinary good English brass 66·6 p.c. (*i.e.* 2 of copper to 1 of zinc); while common cast brass contains about 62 p.c. of copper. A little lead is generally added in preparing cast brass; this gives sounder castings and produces a metal which turns much better in the lathe than ordinary brass. Although not unfrequently as much as 2 p.c. of lead is added to the charge, most of this is removed by oxidation and usually only about 0·3–0·5 p.c. remains. The loss of metal in melting and casting is usually about 5 p.c., but this is greater when much small scrap is used. It may be added that in the preparation of cast brass it is not so necessary to ensure the absence of very small quantities of metals such as antimony, bismuth, and silver as is the case when the alloy has afterwards to be rolled or drawn. When special ductility or malleability is required in the final product, it is of the utmost importance that the purest obtainable materials should be employed.

When alloys of the copper-zinc series are cast in bars in sand moulds, and the length of the bars during cooling is observed by means of an extensometer, it is found that in some cases marked expansion occurs, while with other compositions there is little or no expansion. There are three maxima, which in order of magnitude occur with 15, 80, and 50 p.c. of copper respectively. The series has four maxima on the hardness curve, which are with 40, 80, 65, and 10 p.c. respectively. The 40 p.c. alloy is exceptionally hard (Turner and Murray, J. Inst. of Metals, 1909, 2, 98).

Sheet brass. One of the most important applications of brass is for the production of sheets, as sheet brass is not only needed for a multitude of useful and ornamental purposes itself, but it forms the starting-point for the manufacture of the greater part of the brass wire and tubing that is dealt with in commerce.

For the production of 'yellow metal' it is customary to prepare the alloy by melting copper on the bed of a small reverberatory furnace and adding the requisite quantity of zinc. But in preparing other varieties of sheet brass it is usual to employ crucibles heated in coke fires as described for cast brass. Gas- or oil-fired furnaces are also employed. The crucibles generally hold about 120 lbs. of metal. In either case the alloy when melted is cast in iron moulds into flat bars, varying in size, but of which one about 4½ in. × ⅜ in. × 90 in. may be taken as an example. These are known as 'strips' and the operation is known as 'strip casting.'

The strips are then 'broken down' by being passed cold through a pair of rolls, the operation being repeated as often as the metal will allow. The work done upon the metal soon causes it to become hard, and if the rolling were continued the strip would readily develop cracks. To obviate this the metal is annealed at a red heat and the surface is cleaned from oxide by pickling in dilute sulphuric acid. After washing with water, the operations of rolling, annealing, pickling, and washing are repeated, in order, until the desired shape and thickness are obtained. During the process of rolling the original crystalline structure of the alloy is largely broken down and an amorphous hard matrix is produced. This subject has been fully dealt with by Beilby (Hard and Soft States in Metals, J. Inst. of Metals, 1911, 6, 5). On annealing, the first effect is to restore the crystalline structure of the alloys. At the same time it becomes soft and ductile. If, however, the temperature of annealing be too high, or the time unduly prolonged, the crystals increase in size, and ultimately become so large that the material is quite weak, brittle, and worthless for practical purposes. The proper annealing temperature varies with the composition of the alloy, and the whole question has been studied by Hudson and Bengough (J. Inst. of Metals, 4, 1910, 92), and by Bengough (*ibid.* 7, 1912). With 70·30 p.c. brass the best annealing temperature is between 600° and 700°, but brass may become coarsely crystallised or 'burnt' at 100° below the solidus line if maintained for sufficient time, while it may safely be heated to within a few degrees of the solidus if the time does not exceed half an hour. Turner has shown (Chem. News, 63, 227, 64, 143) that the use of impure washing water containing chlorides leads to the production of copper-red stains and smears, on the surface of the finished brass, which is a cause of frequent loss and trouble. As sheet brass is used for so many purposes, its composition varies over a wide range, extending in fact from a mere trace to 40 p.c. of zinc.

Since the ductility of the alloy increases with the proportion of copper, alloys such as best red brass, gilding metal, and percussion-cap metal contain from 80 to 96 p.c. of copper. Dutch metal contains 80–85 p.c.; Prince's metal, 75 p.c.; best English sheet brass, 70–72 p.c.; ordinary, 66·6 p.c.; common, 63 p.c.; and yellow metal, 60 p.c. As already explained, this last alloy, though somewhat deficient in ductility, is strong and possesses the great advantage that it can be rolled either hot or cold. White metal alloys are used in the form of sheet to a limited extent, and these contain less than 50 p.c. of copper. The cheaper yellow alloys, rich in zinc, do not 'stand the fire' so well in soldering, and it is not usual to solder anything containing less than 60 p.c. copper. Even with this composition a special soft solder has to be employed, whilst red brass stands the fire best, and can be used with the hardest solder.

Brass wire is made from sheet brass, the sheet of suitable thickness being slit into thin strips by cutters, and the strips are then drawn into wire at the draw bench. The chief varieties of wire arranged in order of ductility are as follows:—Red metal, Prince's metal, ordinary, common, and yellow metal. The first two of these were formerly used in the button trade, as in soldering on the shanks with hard solder they 'stood the fire' well. The other varieties can all be soldered with suitable solder of low melting-point, but the difficulty of soldering increases with the proportion of zinc.

Brass tubes. There are two principal methods of producing brass tubes. By the original process, which is still largely employed, sheet brass of the required composition and thickness is cut into strips of the necessary length; the strips are then drawn through a die, which imparts a circular shape, and the edges are soldered together by the use of powdered solder and borax made into a cream with water. Small tubes are soldered by being drawn through a small furnace fired with small coal or coke, but large tubes are now generally united by the use of a gas blowpipe, which gives a local and easily regulated heat. In the second and more modern method of manufacture brass tubes are solid-drawn, and thus the operation of soldering is dispensed with. This process is chiefly employed for large tubes and for tubes of special quality, as the soldered joint in tubes made in the ordinary way is always more brittle than the rest of the material. The soldered joint is also frequently a cause of corrosion in tubes exposed to steam or salt water. For solid-drawn brass tubes a short hollow cylinder of metal is cast in suitable moulds, and by drawing on a mandril, with frequent annealings, this hollow cylinder is gradually elongated to the required dimensions.

Condenser tubes are generally made of 70 p.c. copper, 30 p.c. zinc; or, according to the Admiralty specification, in which 1 p.c. of the zinc is replaced by tin. The corrosion of condenser tubes is a source of considerable loss and trouble, especially in the mercantile marine. The causes which lead to such corrosion have been studied by Bengough (J. Inst. of Metals, 1911, 5, 28) and Brühl (*ibid.* 6, 279).

Ornamental patterns on brass tubes when parallel with the length of the tube are produced by passing the plain tubes through a set of suitably arranged rolls, on the surface of which the desired pattern is cut. But when the pattern is of a spiral form it is usual to draw the plain tube through a die of the requisite shape, arrangements being made for either the tube or the die to rotate during the operation. Best drawn tubes for locomotives and similar purposes contain 70–72 p.c. of copper; the composition of other tubes varies according to the quality of the sheet brass used in the process of manufacture.

Colouring of brass. A considerable proportion of the goods originally made of brass are so coloured before passing into commerce that the tint of the metal itself is no longer to be recognised. The most important applications of colouring are the following:—Bronzing in various shades, such as black, grey, red, green, &c.; lacquering in many shades; and bright colouring with highly coloured, transparent lacquers. These processes of colouring may be divided into two classes according as to whether they are conducted before or during the operation of lacquering.

As has been pointed out by Löwenherz, a variety of shades of colour can be obtained by carefully heating bright clean brass to definite and regulated temperatures. These colours so produced are formed in the following order:

1. Orange yellow.
2. Clear golden yellow.
3. Orange gold.
4. Dark gold.
5. Brown gold.
6. Rose-red gold.
7. Violet-rose red.
8. Clear rose.
9. Steel white.

Some of the colours are of great firmness and beauty, and the process if full of promise for special purposes, but has not hitherto been successfully adopted on any considerable scale.

The methods of bronzing, applied before lacquering, include the following:

Copper bronzing. To develop a copper-coloured surface on brass the metal may be cautiously rubbed with hydrochloric acid, or, still better, it may be immersed in a slightly acid dilute solution of copper nitrate until the desired depth of colour is obtained. To produce a dark copper-bronze colour, treat as above, and blacken the surface with plumbago before lacquering.

Grey bronze. A cheap grey bronze is produced by rubbing with plumbago and using a nearly colourless lacquer. A more permanent grey bronze is produced by the use of a solution of arsenic trioxide in hydrochloric acid; the addition of iron salts improves the effect. For common work, which is *not soldered*, an aqueous solution of mercuric chloride rendered acid with vinegar is frequently used.

Black bronze. The very beautiful and permanent black bronze used for mathematical and scientific instruments is produced by the application of a dilute aqueous solution of platinum tetrachloride which was introduced for this purpose about the year 1860.

Green bronze. A cheap green bronze which was formerly much in favour was obtained by the use of plumbago followed by a transparent yellow lacquer.

Ordinary lacquer is a solution of shellac in proof spirit, but other gums and solvents are also used. A colourless 'dip' lacquer (*i.e.* one in which the articles may be dipped, instead of the lacquer being applied by means of a brush to the warm surface as usual) is made by dissolving nitrocellulose in amylacetate. For ordinary purposes many shades of lacquer from colourless, through yellow, to brown are regularly employed. For the cheaper kinds of bronzing special bronze lacquers of a variety of colours are used; and in addition richly coloured transparent lacquers of numerous shades are produced for the manufacture of brightly coloured thin sheet metal for ornamental purposes. In this branch of manufacture the use of aniline derivatives has led to numerous improvements.

T. T.

Compounds of Zinc.

Zinc oxide ZnO. This substance, the *nix alba*, 'philosophical wool,' or 'flowers of zinc' of the alchemists, the *tutia* or *pompholyx* of the ancients, occurs as the mineral zincite or red zinc ore which is a mixture of zinc oxide and 7–12 p.c. red manganese oxide. It is often found in red or orange-yellow hexagonal crystals or in granular masses. Zinc oxide is occasionally found crystalline in zinc and brass melting furnaces.

Zinc oxide is known in commerce as zinc white, and is generally prepared on the large scale by burning zinc or its ores in retorts, or in an electric furnace, the zinc fumes being led into chambers where they meet a current of air and the oxide thus formed is led into a second chamber and allowed to condense; or the ore may be heated with anthracite or charcoal, and the resulting hot fumes treated with air (*see* Eng. Pats. 16129, 1891; 11233, 1894; 4310, 1894; 12274, 1901; 18015, 1903; 4058, 1904; 21787, 19839, 1906; U.S. Pat. 902260, 1908; Fr. Pat. 403681, 1909; amongst others; J. Soc. Chem. Ind. 1894, 401; *ibid.* 1901, 911; *ibid.* 1903, 1138; *ibid.* 1906, 1056; *ibid.* 1907, 1150; *ibid.* 1910, 88; Schnabel, Eng. and Mining J. 1892, 9, 26295).

Zinc oxide may also be prepared by heating zinc sulphate with carbon for about 2 hours at about 650° (Eng. Pat. 3906; D. R. P. 93315).

A hot solution of sodium sulphate or other alkali salt is electrolysed with zinc electrodes; zinc sulphate is formed at the anode, and sodium hydroxide at the cathode. These react forming zinc hydroxide, which is then calcined (Fr. Pats. 328491, 1903; 348294, 1904; U.S. Pat. 771025, 1903; Ind. Elektrochem. 1904, 8, 20).

The zinc oxide of pharmacy is prepared either by burning the metal or by precipitating very pure zinc sulphate with a hot solution of sodium, magnesium, or other carbonate, and heating the dried carbonate to expel carbon dioxide (Jansen, Mag. Pharm. 26, 74; Dulk, Berl. Jahrb. Pharm. 24, 2, 74; 29, i. 59; D. R. P. 21987, 151022; Rigg, Eng. Min. J. 75, 626).

Crystalline zinc oxide of sp.gr. 5·782 may be obtained by igniting the nitrate (Brügelmann, Zeitsch. anal. Chem. 29, 126); by heating zinc chloride in a stream of water vapour (Daubrée, Compt. rend. 1854, 39, 153); and by a number of other methods (Sidot, *ibid.* 1869, 69, 202; Gorgeu, *ibid.* 1887, 104, 120).

A large number of patents have been taken out for the preparation of the oxide by various methods, of which the following may be mentioned (Fr. Pats. 338977, 1903; 373027, 373953, 1906; 406150, 1908; 404840, 1909; 412214, 411672, 1910; Eng. Pats. 2532, 1905; 24526, 1906; U.S. Pats. 815516, 1906; 899322, 900088, 1908; 919375, 919376, 920336, 920337, 1909; J. Soc. Chem. Ind. 1897, 812; 1899, 1033; 1904, 1034; 1906, 325, 374; 1907, 477; 1910, 223, 425, 1016).

Zinc oxide is a white powder of sp.gr. 5·6 (*see* Fuchs and Schiff, *ibid.* 1896, 363), which, on heating, becomes lemon-yellow, but on cooling again becomes white.

According to Schüpphaus, the yellow colour is due to the formation of a suboxide (*ibid.* 1899, 987). Zinc oxide volatilises in the electric furnace, the vapours condensing in long, transparent crystals (Moissan, Compt. rend. 1892, 115, 1034). In a current of air it commences to volatilise at 1100° (Doeltz, Metallurgie, 1906, 3, 212). At a bright red heat the oxide is probably polymerised to some extent (de Forcrand, Compt. rend. 1902, 134, 1426; *ibid.* 135, 36; Ann. Chim. Phys. 1902, [vii.] 27, 26). Zinc oxide commences to be reduced by carbon in an atmosphere of nitrogen at 800°, by carbon dioxide at 600°, reduction in both cases increasing rapidly with rise in temperature (Doeltz and Graumann, Metallurgie, 1907, 4, 290). By magnesium it is reduced with explosive violence (Winkler, Ber. 1890, 23, 120).

When strongly heated in the oxyhydrogen flame it emits an intense white light, and is seen to phosphoresce when cooled in the dark. The character of the light emitted by incandescent zinc oxide has been examined by E. L. Nichols and B. W. Snow (Phil. Mag. [v.] 32, 420; and [5] 33, 19; *see* also Schmidt, Ann. Physik. 1904, [iv.] 13, 622; Tafel, *ibid.* 14, 206), who have studied the behaviour of zinc oxide under the action of canal rays.

One part of the oxide dissolves in 236,000 of water (Dupré and Bialas, Zeitsch. angew. Chem. 1903, 16, 54). If quite pure it dissolves completely in ammonia. It is readily soluble in acids, forming the corresponding zinc salts which are colourless substances having a disagreeable taste, are often poisonous to plants and animals, act as emetics, and are employed in medicine, chiefly for external application.

Zinc white has been recommended as a useful, efficient, and more healthy substitute for white lead for oil painting, and in the preparation of varnishes (Livache, Compt. rend. 1901, 132, 1230; Bull. Soc. d'Encouragement, 1908, 110, 516; 1902, 103, 690; Lenoble, J. Soc. Chem. Ind. 1904, 829). For this purpose zinc white, alone, or mixed with finely-ground silica and calcium carbonate, is made into an emulsion with linseed or a similar oil (Eng. Pat. 4870, 1893; Fr. Pat. 366465, 1906; D. R. PP. 175402, 178983; J. Soc. Chem. Ind. 1894, 262; *ibid.* 1906, 1056).

A mixture of zinc hydroxide and hydrocarbonate, used as a white pigment, is prepared by intimately pulverising zinc ore with quicklime, then extracting the mixture with liquid ammonia. After removing foreign metals by ordinary methods the ammoniacal liquid is distilled in a vacuum with or without the application of heat (Fr. Pats. 309079, 2001, 1903).

A mixture of ground zinc white and hydrated oxide of zinc precipitated in the cold or at 50°–80°, is said to be a useful enamel pigment when used in the proportions represented by the formula $2ZnO+Zn(OH)_2$, whilst for matt-surface paints the proportion should be $6ZnO+Zn(OH)_2$. As a second coat for enamelling, zinc carbonate may be substituted for a part or the whole of the zinc oxide (Joannis, J. Soc. Chem. Ind. 1906, 486).

Zinc soaps are manufactured by thoroughly mixing about 0·25 p.c. oleic or other aliphatic acid with zinc oxide and a little water. The resulting zinc soap can now be mixed into an emulsion with raw or boiled oil, a thick paste thus being formed, the constituents of which do not separate even on prolonged standing (Fr. Pat. 368755, 1906).

Zinc lead pigment consists of zinc oxide and sulphate, lead oxide and sulphate, some sulphur dioxide and water (Buskett, Eng. and Ming. J. 1907, 83, 760).

Zinc oxide is used in the manufacture of cements (D. R. P. 56958; Fr. Pats. 332788, 333671, 1903). When mixed with aluminium phosphate it is used as a dental cement (Grenet, Chem. Zeit. 1909, 33, 610).

It is also employed in the glass industry (J. 1894, 151, 354; Zschimmer, Chem. Zentr. 1907, ii. 1461; Walker, J. Amer. Chem. Soc. 1905, 27, 865); and in the preparation of crystalline glazes (Holdcroft, Trans. Eng. Ceramic Soc. 1909–10, 9, 37).

Crystalline zinc glazes are formed by the separation of zinc silicate on slow cooling of the glaze. It has a smaller coefficient of expansion than other glazes, and when melted on to pottery or stoneware is less liable to 'craze' than lead glaze.

By addition of different oxides, characteristic colour effects can be obtained with zinc glazes. Zinc oxide may also be used in place of the more costly tin oxide for producing opalescent glazes (Petrik, Chem. Zeit. 1908, 32, Rep. 490).

Crystalline zinc glazes are prepared by mixing 27·389 parts by weight of zinc oxide with 7·382 potassium nitrate, 13·770 borax, 7·200 whiting, 4·466 flaky boric acid, 0·600 cupric oxide, and 39·693 flint. The glaze should be ground as finely as possible and applied to the surface to be glazed with dextrin as an adhesive (Riddle, Trans. Amer. Ceramic Soc. 1906, 8, 336; Minton, *ibid.* 1907, 9, 782). It is also used for the production of white and colour resists employed in printing processes (Lauber, Zeitsch. Farben. and Textil Ind. 1904, 3, 417); for the preparation of certain sizing materials (D. R. P. 194726; J. Soc. Chem. Ind. 1908, 634); and to some extent in analytical processes in the laboratory (Meineke, Zeitsch. angew. Chem. 1888, 252; Koninck, Chem. Zeit. 1905, 29, Rep. 5).

For the estimation of zinc oxide in zinc paints and lithopones, *see* J. Soc. Chem. Ind. 1907, 977; Stromeyer, Arch. Pharm. 27, 549.

Zinc grey is obtained as a by-product in the manufacture of zinc white. Made into a paste with wood oil it is used as a cement for steam joints (Livache, Bull. Soc. d'Encouragement, 1905, 107, 568). It also forms a good, silver grey oil paint.

Zinc hydroxide $Zn(OH)_2$ is obtained as a white powder by adding caustic potash or soda or ammonia to a solution of a zinc salt. It may be obtained crystalline by allowing zinc to remain in contact with iron or copper under a layer of ammonia or by allowing its saturated solution in caustic potash to stand, or by the action of water on zinc oxide (de Forcrand, *l.c.*). It is stable in air up to 85°, loses nearly all its water at 130°–140°, is readily soluble in excess of ammonia and alkalis towards which it behaves as the weak acid, H_2ZnO. (Herz, Zeitsch. anorg. Chem. 1901, 26, 90; Rubenbauer, *ibid.* 1902, 30, 331; Hantzsch, *ibid.* 289; Bonsdorff, *ibid.* 1904, 41, 132; Moir, Chem. Soc. Proc. 1905, 310; Dawson and McCrae, Chem. Soc. Trans. 1900, 1239; Euler, Ber. 1903, 36, 3400; Kuriloff, Zeitsch. Elektrochem. 1906, 12, 209; Bull. Acad. St. Petersburg, 1901, 1, 95). A mixture of zinc ammonium hydroxide and copper ammonium hydroxide has been used for pectinising cellulose and similar substances to produce a kind of vegetable parchment (J. Soc. Chem. Ind. 1884, 122).

Zinc peroxide ZnO_2, also known under the trade names *Zinkonal*, *Dermogen*, *Ektogan*, and *Zinc perhydrol*, is formed by the action of hydrogen peroxide on zinc oxide or hydroxide (Kuriloff, J. Russ. Phys. Chem. Soc. 1890, 22, 171; de Forcrand, Compt. rend. 1902, 134, 601; *ibid.* 135, 103; D. R. P. 171372). It has also been formed by subjecting an aqueous solution of barium peroxide to the action of a zinc salt, the acid radicle of which forms a soluble salt with barium (U.S. Pats. 709086, 1902; 740832, 1903), or better, by the electrolysis of a zinc chloride solution contained in a vessel with a porous diaphragm, hydrogen peroxide being added to the cathode compartment and platinum or carbon being used as anodes and platinum or tin as cathodes (D. R. P. 151129; for another method *see* J. Soc. Chem. Ind. 1905, 947; also Fr. Pat. 364825, 1906). A number of peroxides have been described, but, according to Kuriloff (Compt. rend. 1903, 137, 618; *see* also de Forcrand, *ibid.* 1904, 138, 129), the only one which is a definite chemical compound has the composition $ZnO_2,Zn(OH)_2$, the others all being mixtures of varying quantities of zinc peroxide with zinc oxide or zinc hydroxide (Lemaire, Rép. Pharm. 1910, 22, 1; Foregger and Philipp, J. Soc. Chem. Ind. 1906, 298).

Zinc peroxide is a yellowish-white, tasteless, odourless, non-hygroscopic, antiseptic, non-irritant powder. It is stable in the autoclave to 130°, and at a dry heat to 150°, is insoluble in water, and gives all the ordinary reactions of a peroxide.

Mixed with tartaric acid it is applied as a dressing to wounds, chronic ulcers, &c. It thus liberates hydrogen peroxide *in situ*, and is therefore more active than the same quantity of the latter applied in the usual way. For eczema and other skin diseases it is applied, mixed with half its weight of potassium iodide and some tartaric acid (Chem. Zentr. 1906, ii. 548; D. R. PP. 14821, 157737; Homeyer, Apoth. Zeit. 1902, 17, 697; J. Soc. Chem. Ind. 1905, 947).

Zinc chloride $ZnCl_2$, the *oleum lapidis calaminaris* of Glauber, who first described it in 1648, may be prepared in the anhydrous state by distilling zinc oxide with sal-ammoniac, forming the ‘butter of zinc’ of Hellot; by distilling zinc with corrosive sublimate (Pott); by the action of chlorine on the metal (Westrumb), or by heating dehydrated zinc sulphate with calcium chloride (Persoz) (Eng. Pat. 982, 1892; 15813, 1895; D. R. PP. 154518, 158089).

On the large scale it is usually obtained by placing scrap zinc in a stone, cast iron, or wooden vessel containing hydrochloric acid. The solution is neutralised with sodium carbonate, warmed to 40° or 50°, and mixed with bleaching powder to precipitate iron and manganese. The clear zinc chloride solution is siphoned off and boiled down in enamelled iron pots. The evaporation is continued until the temperature of the liquor is 230° or 240°, a little potassium chlorate is added to oxidise any organic matter, and some pure hydrochloric acid carefully poured into the hot solution to dissolve any basic salt. The mass is then allowed to solidify, the agitation being kept up all the time, and while still warm it is packed in iron drums of 30–50 kilos. capacity, which are at once closed air-tight.

According to a more recent patent (Fr. Pat. 385448, 1907), zinc-bearing material is intimately mixed with sawdust or similar substance containing cellulose in earthenware or cast-iron twin tubular retorts, which are used alternately. The first retort is heated to 120°–130°, and chlorine is passed in at the base, hydrochloric acid is thus generated *in situ*, and the temperature rises spontaneously to 230°–250°. The products of combustion pass from the upper part of the retort to a receptacle where the tar is deposited and thence to the base of the second retort where the excess chlorine is fixed and the products then pass out into a second receptacle, where the tar is again fixed, and thence into a coil and receiver cooled by water. The mass thus obtained is lixiviated with water. Iron and manganese are then oxidised with chlorine and calcium hypochlorite, the iron is precipitated by zinc oxide, the manganese, if necessary, by lead peroxide (D. R. PP. 154085; 136521), and the other metals by agitation with zinc. The remaining liquor is then finally evaporated to obtain pure zinc chloride.

It may also be obtained almost pure by treating zinc compounds with ferrous chloride (D. R. P. 136521); by heating zinc ore to 550°, passing hydrogen chloride over it, and finally lixiviating the mass so obtained (D. R. P. 158087). A large number of patents exist for the preparation and purification of zinc chloride by the above and other methods (Eng. Pats. 22826, 22827, 1894; 5662, 8449, 7561, 1895; 24573, 1896, 19878, 1900; D. R. PP. 155065. 172460; U.S. Pats. 845868, 1907; 883426, 1908; Mallet and Guye, Chem. Zeit. 1904, 28, 763; J. Soc. Chem. Ind. 1893, 276; *ibid.* 1895, 450, 595; *ibid.* 1896, 198, 356; *ibid.* 1897, 1015; *ibid.* 1900, 146; *ibid.* 1905, 497).

Pure anhydrous zinc chloride can be prepared by dissolving 40 grms. of the chloride in 20 c.c. of hydrochloric acid (sp.gr. 1·19), and evaporating the solution in a tube of refractory glass through which a stream of hydrogen chloride is passed. The temperature is gradually raised, and after some time the mass solidifies with evolution of hydrogen chloride. The solid chloride is fused again rapidly in a current of the same gas. The dehydration is complete in 75 mins. (Grünauer, Zeitsch. anorg. Chem. 1904, 39, 389; *see* Vogel, Faraday Soc. Trans. 1906, May 5; *see* also D. R. P. 120970).

Zinc chloride is a white or greyish-white mass or powder, of sp.gr. 2·907 at 25°/4° (Baxter and Lamb, Amer. Chem. J. 1904, 31, 229). Its m.p. is variously given as 100° (Davy), 250° (Lorenz), 262° (Braun, Mylius, and Dietz), 290°–300° (Schulze). According to Grünauer the completely anhydrous chloride has m.p. 365°. It is very hygroscopic and deliquescent, odourless, poisonous, with a metallic astringent taste. It melts to a clear, mobile, highly refractive liquid, b.p. 730°–732°; in a current of chlorine it sublimes, forming acicular crystals. It forms hydrates with 1, 1·5, 2·5, 3, and 4 molecules of water (Dietz, Ber. 1899, 32, 90; Mylius and Dietz, *ibid.* 1905, 38, 921). Its aqueous solution dissolves paper and cotton, and it should therefore be filtered through asbestos or glass, not paper. When evaporated or boiled with zinc oxide, oxychlorides are formed (Perrot, Bull. Soc. chim. 1895, [iii.] 13, 975; Driot, Compt. rend. 1910, 150, 426), whilst if a solution of sp.gr. 1·7 be boiled with an excess of zinc oxide, the resulting liquid dissolves silk, and can be employed for separating the latter from wool, cotton, or linen. Zinc oxychloride is sometimes also used in the preparation of some dental cements, and as a pigment.

When zinc chloride is electrolysed, chlorine is evolved and crystalline zinc is deposited (Saposhnikoff, J. Russ. Phys. Chem. Soc. 1905, 37, 153; *see* also Schultze, Zeitsch. anorg. Chem. 1899, 20, 323; Grünauer, *l.c.*).

Zinc chloride comes into pharmacy in the form of rods or tablets. It is a powerful caustic, distinguished by its property of burning deeply and not spreading sidewise. It is applied in substance, or made into a paste with starch or gypsum, to cancers, sloughing or unhealthy sores, and nævi (Lauder Brunton).

In dilute solution it is also used as an astringent, an antiseptic, a disinfectant, and as a deodorant.

A solution of zinc chloride, in the proportion of 1 lb. of the salt to 5 gallons of water, was patented by Sir W. Burnett (Eng. Pat. 7747, 1838) for the preservation of timber, and such a solution is still occasionally used for disinfecting and deodorising.

For the preservation of wood it has been recommended to employ an emulsion of aqueous zinc chloride, and wood-tar oil (D. R. PP. 139441, 152179; Chem. Zentr. 1903, i. 749; *ibid.* 1904, ii. 379); or a 15 p.c. solution of a mixture of ammonium sulphate and a soluble zinc salt (D. R. P. 109324).

Zinc chloride is employed for weighting cotton goods (Furth, Färber Zeit. 1901, 12, 1; D. R. P. 214372, 215702; Chem. Zentr. 1909, ii. 1508, 1905), and for crimping cotton, wool, and silk (Bull. Soc. Ind. Mulhouse, 1898, 68, 350, 348; *see* also Flintoff, J. Soc. Dyers, 1899, 15, 151).

Solutions of zinc chloride were also employed by Mercer for treating cotton in the operation of 'mercerising' (*v.* CELLULOSE).

Zinc chloride dissolves casein and these solutions have been employed for preparing artificial silk and hair. Zinc chloride has also been used in the production of hydrochloric acid from hydrogen and chlorine (Fr. Pat. 352419; Chem. Zeit. 1905, 29, 993); for the prevention of the rusting of iron (Reed, Trans. Amer. Electrochem. Soc. 1903, 3, 149); in the preparation of glass etching liquids (J. 1894, 354), and in the laboratory as an analytical, dehydrating and condensing agent and in the synthesis of a large number of organic compounds (Kondakoff, J. Russ. Phys. Chem. Soc. 1892, 24, 114, 309; J. pr. Chem. [ii.] 48, 467; Dott, Pharm. J. 1905, [iv.] 21, 136; among others).

Zinc chloride forms double chlorides with the alkali and other metals (Wells and Campbell, Zeitsch. anorg. Chem. 1894, 5, 273; Ephraim, *ibid.* 1908, 59, 756; Ephraim and Model, *ibid.* 1910, 67, 376, 379; Baxter and Lamb, *l.c.*; Gewecke, Annalen, 1909, 366, 217), with copper oxide (Mailhe, Compt. rend. 1901, 133, 226), an *iodo chloride* $ZnCl_2 2ICl_3,8H_2O$ (Weinland and Schlegelmilch, Zeitsch. anorg. Chem. 1902, 30, 134), a *chlorobromate* (Löwenthal, *ibid.* 1894, 6, 355), and a *chloroborate* $6ZnO,8B_2O_3,ZnCl_2$ (Rousseau and Allaire, Compt. rend. 1894, 118, 1255). Zinc chloride also forms double compounds with ammonia, such as $ZnCl_2{\cdot}NH_3$, $ZnCl_2{\cdot}2NH_3$ (Thoms, Chem. Zentr. 1889, ii. 965; Kwasnick, Arch. Pharm. 229, 310; Jaeger, Ber. 1902, 35, 3405), and with ammonium chloride (Curtius and Schrader, J. pr. Chem. 1894, [ii.] 50, 311; Meerburg, Zietsch. anorg. Chem. 1903, 37, 199).

A solution of zinc ammonium chloride is used in soldering for the purpose of removing oxide from the surface of the metals.

Zinc bromide $ZnBr_2$ is readily made by digesting granulated zinc with bromine water. It resembles the chloride, and is used to a small extent in medicine in the treatment of epilepsy.

Zinc iodide ZnI_2 is also employed in medicine, as an application to enlarged tonsils and in the form of ointment to reduce swellings. It is also administered internally in cases of scrofula, chorea, and hysteria. It has found a limited application in photography.

For a number of double compounds of the bromide and iodide with other metallic compounds, *see* Ephraim, *l.c.*; Ephraim and Model, *l.c.*; Rousseau and Allaire, Compt. rend. 1893, 116, 1445; *ibid.* 119, 71; Tassiliy, *ibid.* 1896, 123, 323; Duboin, *ibid.* 1906, 143, 40; Chrétien, Ann. Chim. Phys. 1898, [vii.] 15, 358; Mosnier, *ibid.* 1897, [vii.] 374.

Zinc fluoride ZnF_2 is formed by the action of hydrofluoric acid on zinc or on zinc oxide at a red heat, or on zinc chloride at 800°–900° (Poulenc, Compt. rend. 1893, 116, 581). It forms slender, colourless, transparent needles, sp.gr. 4·84 at 15°, sparingly soluble in cold water, soluble in boiling mineral acids. It is reduced by hydrogen at a red heat; when heated in air it forms zinc oxide. When dissolved in hydrofluoric acid, or when zinc is dissolved in excess of hydrofluoric acid, it forms the compound ZnF_2,HF, which has been recommended for use in the preservation of wood, particularly of telegraph poles (Nowotny, Chem. Zentr. 1908, ii. 355). Like the other halides, zinc fluoride yields a number of double salts (Helmolt, Zeitsch. anorg. Chem. 1893, 3, 115; Weinland and Köppen, *ibid.* 1899, 22, 266; Giorgis, Gazz. chim. ital. 22, i. 55; Higley, J. Amer. Chem. Soc. 1904, 26, 613; Rimbach and Kilian, Annalen, 1909, 368, 101).

Zinc sulphate $ZnSO_4$. This salt has long been known under the name which it still bears, of 'white vitriol.' It was obtained, on a manufacturing scale, as far back as the sixteenth century, by lixiviating roasted zinc sulphide by means of water, and crystallising the solution—a method still practised, with certain modifications (U.S. Pat. 851639, 1907; J. Soc. Chem. Ind. 1907, 608).

In some processes the zinc pyrites is previously treated with sulphuric acid, after which it is roasted (D. R. P. 154518). It is then sometimes further treated with oxidising agents. In some cases again the ore is treated with a mixture of dilute sulphuric acid, ferric sulphate, and a little sodium chloride (D. R. P. 197044), or with ferric sulphate alone (D. R. P. 200613). According to D. R. P. 135056, after converting the sulphide ore into the sulphate in the ordinary way, the product is roasted with calcium hydroxide and sodium nitrate in a muffle furnace in order to drive off the impurities, or to convert them into insoluble compounds. When the process is finished, the zinc sulphate is lixiviated out (*see* also D. R. PP. 120822, 135182; Knokloch, Pharm. Zeit. 40, 472; Hofmann, Amer. Inst. Mining Eng. Trans. 1905, 117; Fr. Pat. 384904, 1907).

Native zinc sulphate or *goslarite* is occasionally found in zinc mines, being probably formed by the oxidation of zinc sulphide.

Zinc sulphate separates from its solution at the ordinary temperature in right rhombic prisms, isomorphous with magnesium sulphate, and of the composition $ZnSO_4,7H_2O$; sp.gr. 1·95; 2·036 (Mohs). It has a strong metallic styptic taste, and effloresces slightly in dry air. According to Poggiale, 100 parts of water dissolve the following amounts of zinc sulphate at different temperatures (*see* also Callendar and Barnes, J. Phys. Chem. 1897, 2, 536, who give slightly different figures):—

	$ZnSO_4,7H_2O$	Anhydrous salt
10° . .	138·2 . .	48·3
20° . .	161·5 . .	53·1
30° . .	191·0 . .	58·5
50° . .	263·8 . .	68·7
100° . .	653·6 . .	95·6

The solution has an acid reaction and is poisonous. The salt is insoluble in absolute alcohol.

Solutions of zinc sulphate keep clearer in the light than in dark (Verda, Chem. Zentr. 1907, i. 1392).

A hexahydrated salt $ZnSO_4,6H_2O$ is obtained by crystallising the solution at 40°; sp.gr. 2·072 (Thorpe and Watts); a pentahydrated salt $ZnSO_4,5H_2O$ by boiling the salt with alcohol of sp.gr. 0·825 (sp.gr. 2·206, Thorpe and Watts), and a dihydrated salt by pouring a cold saturated solution of zinc sulphate into strong sulphuric acid, and washing the precipitate with absolute alcohol until free from uncombined acid; sp.gr. 2·958 (Thorpe and Watts). The monohydrated salt is formed by heating the heptahydrated salt to 110° until it ceases to lose weight; sp.gr. 3·284 (Thorpe and Watts). The anhydrous salt is obtained by heating the heptahydrate to 300°; sp.gr. 3·4. At a red heat all the sulphates are decomposed, yielding a residue of zinc oxide.

Zinc sulphate is used in dyeing and calico-printing, in the manufacture of varnishes and drying oils for painting.

Coloured zinc pigments are prepared by intimately mixing together zinc sulphate with 6–30 p.c. of the sulphate of other metals which yield a coloured oxide, such as nickel, iron, cobalt, or manganese. The mixture is dried, finely divided carbon is added, and the whole ignited carefully at 650°. To produce a more delicately-tinted pigment, the zinc sulphate should first be purified by stirring zinc oxide into its solution and passing a current of chlorine through it, whereby the impurities are thrown down (Eng. Pat. 17031, 1896; Fr. Pat. 366517, 1908; J. Soc. Chem. Ind. 1908, 1074).

It is also used for the preparation of zinc white and other zinc compounds, and in pharmacy as an astringent, and in lotions, washes, and gargles. It is also occasionally employed as an emetic, and in the treatment of convulsive diseases. A number of basic sulphates, formed by digesting the oxide or hydroxide with strong solutions of zinc vitriol, or precipitating such solutions with varying quantities of potash, can be formed.

Zinc sulphate combines with ammonia and with other sulphates to form double salts (Curtius and Schrader, *l.c.*; Tröger and Ewers, Arch. Pharm. 235, 644; Mallet, Chem. Soc. Trans. 1900, 220; Tutton, *ibid.* 1905, 1123; Koppel, Zeitsch. physikal. Chem. 1905, 52, 385).

The compound $ZnSO_4,3H_2SO_4$ has been separated from the acid in the first chambers in the manufacture of sulphuric acid from zinc blende (Hoffmann, Zeitsch. angew. Chem. **1910**, 23, 1672).

Zinc hydro- or **hyposulphite** ZnS_2O_4 is obtained by passing a current of sulphur dioxide into a mixture of zinc-dust and alcohol or water at a temperature above 40°. On stirring, a crystalline paste of the hydrosulphite is formed, which is washed with methylated spirits and dried *in vacuô* below 70° (Eng. Pat. 3811, 1907; D. R. PP. 184564, 103403, 137494, 144281; Fr. Pat. 331095, 1903; Brunck, Annalen, 1903, 327, 240; Bazlen, Ber. 1905, 38, 1061).

Soluble double salts of zinc hydrosulphite with ammonium salts are obtained by the action of zinc-dust on alkali disulphite in the presence of acid and an ammonium salt (D. R. P. 203846, 1907).

Zinc hydrosulphite forms microscopic rhombic crystals, very soluble in water, giving, very readily, supersaturated solutions. It is employed as a reducing agent in the indigo dyeing industry.

Zinc sulphite $ZnSO_3$ is formed by the action of sodium sulphite on zinc sulphate (Denigès, Bull. Soc. chim. 1892, [iii.] 7, 569). It forms a number of hydrates, double salts and basic salts (Seubert, Arch. Pharm. 1891, 229, 316; Seubert and Elten, Zeitsch. anorg. Chem. 1893, 4, 61; Rammelsberg, Pogg. Ann. 67, 255).

It is used to a very limited extent in medicine.

Zinc sulphide ZnS, as blende, is one of the most important ores of zinc (Robertson, Amer. J. Sci. 40, 160). Its value as an ore of zinc was first demonstrated by Brandt in 1735, it being formerly regarded as a worthless lead ore, *galena inanis*. It is found crystallised in forms derived from the regular system, usually of a red, brown, or black colour, due to the presence of foreign metals. Occasionally it is met with of a light-yellow colour; sp.gr. 3·5–4·2.

It is obtained artificially as a white amorphous precipitate by adding an alkaline sulphide or sulphuretted hydrogen to a solution of a zinc salt (Eng. Pats. 396541, 25965, 1908).

It may also be obtained by dissolving zinc in an alkali hydroxide and then adding just sufficient alkali sulphide to precipitate the zinc (Fr. Pats. 353496, 353480); or by passing zinc chloride vapour over barium or stannous sulphide (Fr. Pat. 338322, 1903; Viard, Compt. rend. 1903, 136, 892).

A mixture of zinc sulphate (230 lbs.), water (90 gallons), ammonia of sp.gr. 0·91 (230 lbs.) is introduced into an enamelled digester and about 60 lbs. of carbon disulphide are added. The vessel is closed and heated to 100° with constant stirring, until the pressure is about 60 lbs. After 4 hours the pressure begins to fall, and in 10 hours it will have fallen to about 22 lbs., when the process is complete. The zinc sulphide is collected, washed, and dried. It is very finely divided and is suitable for use as a pigment (Eng. Pat. 11108, 1900).

Zinc sulphide is sometimes separated from its ores by immersing the crushed ore in a solution of sodium sulphate, disulphate or nitrate, and skimming off the sulphide which rises to the surface (Eng. Pat. 26279, 1902; 27132, 1903; 20160, 20169, 1904; U.S. Pat. 780281; Fr. Pat. 326866, 326867, 1902). For other methods of preparing the sulphide, *see* Eng. Pat. 16272, 1902; Fr. Pats. 397631, 396541, 1908; 415605, 1910; D. R. PP. 132916, 137801, 149557, 167172, 167498, 171872, 179022).

Zinc sulphide is soluble in dilute mineral acids, but is insoluble in acetic acid. When heated in a stream of sulphuretted hydrogen, or in an electric furnace, it forms hexagonal crystals identical in form with a naturally occurring variety known as *wurtzite* (Mourlot, Compt. rend. 1896, 123, 54; Traube, Jahrb. Min. 9, 147). This is also formed when zinc oxide is ignited in sulphuretted hydrogen. For other methods of converting the amorphous sulphide into the crystalline variety, *see* Villiers, Compt. rend. 1895, 120, 97, 149, 322, 498; Viard, *ibid. l.c.*; Spring, Zeitsch. physikal. Chem. 1895, 18, 553; Staněk Zeitsch. anorg. Chem. Chem. 1898, 17, 124.

Pure zinc sulphide melts at 1600°–1700°, and is distinctly volatile at higher temperatures (Friedrich, Metallurgie, 1908, 5, 114). According to Krutwig (J. Soc. Chem. Ind. 1906, 267) the precipitated sulphide decomposes much more readily than natural zinc blende. When treated with hot concentrated sulphuric acid, zinc sulphide evolves sulphur dioxide, whilst with the cold dilute acid, sulphuretted hydrogen is formed (Berthelot, Ann. Chim. Phys. 1898, [vii.] 14 176). Zinc sulphide may be completely reduced by heating it with spongy metallic iron at 1300° (Graumann, Metallurgie, 1907, 4, 69). Freshly precipitated zinc sulphide dissolves in potassium cyanide forming a double salt which is precipitated on boiling (Berthelot, Compt. rend. 1899, 128, 711).

When zinc sulphide is heated with carbon in nitrogen at 1300°–1400°, a volatile compound is formed, which, if the containing vessel is of quartz, reacts with the silicon forming a volatile compound $ZnSSi$, which may also be obtained by heating zinc sulphide with silicon at 1300°. The compound $ZnSSi$ forms hard brown crusts of homogeneous structure. It may be polished like a metal, has an electrical conductivity less than silicon, reacts with acids forming sulphuretted hydrogen and with alkalis with evolution of hydrogen (Fraenkel, Metallurgie, 1909, 6, 682).

Natural zinc sulphide crystals have the property of phosphorescing after exposure to light (Mourelo, Compt. rend, 1899, 128, 557; Verneuil, *ibid.* 1888, 106, 1104), and the phosphorescent sulphide may be prepared artificially by heating precipitated zinc sulphide to redness in the presence of alkali chlorides or the sulphides of other metals (Eng. Pat. 385096, 1907; D. R. P. 163648; Henry, Compt. rend. 1892, 115, 505; Grüne, Ber. 1904, 37, 3076; Hofmann and Ducca, *ibid.* 3407; Jorissen and Ringer, *ibid.* 3983; Chem. Zentr. 1906, i. 644; *see* also D. R. P. 200998). The pure sulphide, however, shows no phosphorescence. It has been proposed to use this property of zinc sulphide in the construction of an actinometer and for photometric purposes (Henry, Compt. rend. 1899, 128, 94). The phosphorescent sulphide glows when exposed to X- or to Becquerel rays; to the α- radiation from radium (Chem. News, 1903, 157; Becquerel, Compt. rend. 1904, 137, 629; Bumstead, Phil. Mag. 1908, [vi.] 15, 432), and under the influence of ozonised oxygen (Schenck and Mihr, Ber. 1904, 37, 3464). When zinc sulphide is heated with manganese nitrate and a number of other substances at 1200°, the product exhibits triboluminescence (Karl, Compt. rend. 1907, 144, 841).

Zinc sulphide may be obtained in a colloidal form by allowing it to remain in contact with water (Donnini, Gazz. chim. ital. 1894, 24, i. 219; Hausmann, Zeitsch. anorg. Chem. 1904, 40, 110); or by allowing a mixture of zinc sulphate, glycerol, and ammonium sulphide to stand for 3 days (Müller, Chem. Zeit. 1904, 28, 357), and in other ways.

Zinc sulphide, or a mixture of zinc sulphide and oxide, is used as a pigment. Griffiths' 'patent zinc white' is obtained by the addition of a soluble sulphide to zinc chloride or sulphate solution, drying the precipitate, and calcining it. It is raked out whilst hot into cold water, and levigated (J. Soc. Chem. Ind. 1885, 563).

A light-proof and weather-proof pigment may be obtained by precipitating zinc as a hydrated sulphide from an alkaline solution. The precipitate is then dehydrated at 300° until $ZnS : H_2O = 5 : 1$ (U.S. Pat. 884874, 1908; *see* also Griffiths' Eng. Pat. 750, 1883; Knight, Eng. Pat. 16220, 1884; J. B. Spence, Eng. Pats. 13462, 1885; 14128, 1885; 27426, 1907; Fr. Pat. 373027, 1906; Cowley, Chem. News, 1891, 63, 88; J. Soc. Chem. Ind. 1910, 99, 166).

A mixture of zinc sulphide and barium sulphate with some zinc oxide is known as *lithopone* or *zincolith.* It is obtained by precipitating hot concentrated zinc sulphate solution with barium sulphide. Rather less than 1 p.c. freshly-precipitated magnesium hydroxide and common salt are added and the precipitate is then washed, dried, crushed, mixed with 3 p.c. ammonium chloride, and heated. The mass, while still hot, is thrown into cold water, after which it is again dried and ground (Leyfert, Zeitsch. angew. Chem. 1902, 15, 802). It comes into commerce in different grades: yellow seal contains 11–18 p.c. ZnS, blue seal 22–30 p.c. ZnS, and green seal, 32–42 p.c. ZnS (Fr. Pats. 335115, 1903; 335358; U.S. Pat. 740072, 1903; Eng. Pats, 1836, 1837, 3768, 3769, 6521, 1903; D. R. PP. 199493, 202420, 163455, 167772, 202253. 202709; Riederer, J. Soc. Chem. Ind. 1909, 403).

Zinc carbonate $ZnCO_3$ occurs native as *smithsonite, calamine* or *zinc spar.* It can be formed artificially by adding zinc sulphate solution to a solution of sodium hydrogen carbonate (Kraut, Zeitsch. anorg. Chem. 1896, 13, 1; Eng. Pat. 6752, 1902; Fr. Pats, 325587, 1902; 329079, 1903; 315888, 1901; J. Soc. Chem. Ind. 1902, 1457; *ibid.* 1903, 214, 752, 1007; Feist, Arch. Pharm. 1909, 247, 439). When the normal carbonate is employed, basic zinc carbonates are formed, the proportion of zinc oxide varying with the temperature and dilution of the solutions. The *zinci carbonas* of the British Pharmacopœia has the approximate composition $ZnCO_3(ZnO)_2,3H_2O$. At a red heat it loses carbon dioxide and forms zinc oxide.

According to Barbier basic zinc carbonate can be effectively employed as a pigment instead of white lead (Fr. Pat. 339151, 1903). It is prepared for this purpose by the electrolysis of a calcium carbonate solution with zinc as anode and carbon as cathode.

Zinc carbonate is a mild astringent to the skin, and is employed in dusting powders and lotion with, or instead of, zinc oxide.

According to Mikusch (Zeitsch. anorg. Chem. 1908, 56, 365) the only basic carbonate of zinc which exists is $5ZnO,2CO_2,4H_2O$. All the others that have been described are solid solutions of zinc oxide and carbonate.

Zinc trithiocarbonate ammonia $CS_3Zn(NH_3)_2$ (Hofmann, Zeitsch. anorg. Chem. 1897, 14, 263); and **dihydroxylamine carbonate**

$$Zn(NH_3O)_2CO_3$$

(Goldschmidt and Syngros, *ibid.* 1894, 5, 129) have been described.

Zinc cyanide $Zn(CN)_2$ is prepared by precipitating zinc acetate with aqueous hydrocyanic acid or by heating zinc-dust with an organic substance containing nitrogen (Aufschläger, Monatsh. 1892, 13, 268). It is a white powder insoluble in alcohol and water, and has been used in the manufacture of alkali cyanides (D. R. P. 132294; Chem. Zentr. 1902, ii. 80). It forms double salts such as $M_2Zn(CN)_4$ and $MZn(CN)_3$ (Berthelot, Ann. Chim. Phys. 1899, 17, [vii.] 458; Sharwood, J. Amer. Chem. Soc. 1903, 25, 570; *see* also Miller and Danziger, *ibid.* 1902, 24, 823; Fischer and Cuntze, Chem. Zeit. 1902, 26, 872). It also combines with ammonia (Varet, Compt. rend. 1887, 105, 1070; *ibid.* 1888, 106, 1080; Ann. Chim. Phys. 1897, [vii.] 10, 5).

Zinc nitrate is formed by dissolving zinc in nitric acid. It is said to crystallise with 2, 3, 4, 6, and 9 molecules of water (Funk, Zeitsch. anorg. Chem. 1899, 20, 400; Vasilieff, J. Russ. Phys. Chem. Soc. 1909, 41, 744, 748). When heated for some time at 100° it forms basic salts (Athanasescu, Bull. Soc. chim. 1896, [iii.] 15, 1078; Terreil, *ibid.* 7, 553; Riban, Compt. rend. 1892, 114, 1357). It also forms double salts (Urbain and Lacombe, *ibid.* 1903, 137, 568).

Zinc nitrite forms fine unstable needles (Matuschek, J. Soc. Chem. Ind. 1902, 705), and also gives double salts (Rosenheim and Oppenheim, Zeitsch. anorg. Chem. 1901, 28, 171).

Zinc nitride Zn_3N_2 is formed by heating zincamide to dull redness, or zinc in a current of ammonia at 600° (White and Kirschbraun, J. Amer. Chem. Soc. 1906, 28, 1343). It is a green powder which becomes incandescent when moistened with water.

Zincamide or **zinc diamine** $Zn(NH_2)_2$ is a white amorphous powder readily decomposed by water, thus:

$$Zn(NH_2)_2+2H_2O=Zn(OH)_2+2NH_3.$$

It is formed by the action of dry ammonia on zinc ethyl (Frankland, Phil. Mag. [iv.] 15, 149).

Zinc hydroxylamine $Zn(O{\cdot}NH_2)_2,3NH_2OH$ is prepared by the action of anhydrous hydroxylamine on finely-divided pure zinc and treating the product with absolute alcohol. It forms glistening crystals which detonate and evolve ammonia when heated rapidly (Ebler and Schott, J. pr. Chem. 1908, [ii.] 78, 289).

Basic **Zinc azoimide** N_3ZnOH (?), *see* Curtius and Rissom, J. pr. Chem. 1898, [ii.] 58, 261.

Zinc borate or **hydroxyborate** $Zn_3(B_4O_7)_2(OH)_2$ is prepared by precipitating an aqueous solution of zinc sulphate (500 grms. salt to 5–10 litres water) by the gradual addition, with constant stirring, of 443·6 grms. of borax solution, and 309 grms. 15 p.c. sodium hydroxide solution. The precipitate is then washed and dried (Holdermann, Arch. Pharm. 1904, 242, 567; *see* also Ouvrard, Compt. rend. 1900, 130, 335; Chatelier, *ibid.* 1891, 113, 1034; Borchers, Zeitsch. anorg. Chem. 1910, 68, 269). It is employed in the preparation of zinc powder for wounds.

Zinc perborate is obtained by the action of sodium peroxide or its hydrate and boric acid, or sodium perborate on a zinc salt or from basic acid and zinc peroxide hydrate. It is a white, amorphous powder applicable to dermatology (D. R. PP. 165278, 165279).

Zinc boracite $6ZnO,8B_2O_3ZnI_2$ is formed by passing a stream of carbon dioxide laden with iodine over a heated mixture of zinc and zinc borate (Allaire, Compt. rend. 1898, 127, 555).

Zinc phosphide Zn_3P_2 is obtained as a crystalline friable mass with metallic lustre, by heating zinc in phosphorus vapour in an atmosphere of dry hydrogen; or by passing a mixture of hydrogen phosphide and nitrogen over zinc heated to redness. It is insoluble in water and in alcohol, soluble in acids with evolution of hydrogen phosphide. Zinc phosphide possesses all the properties of free phosphorus, but is very stable and is used in medicine in place of the latter.

Jolibois (Compt. rend. 1908, 147, 801) has also prepared the phosphide ZnP_2 (*see* also Renault, *ibid.* 1873, 76, 283). For zinc phosphates and other compounds of zinc and phosphorus, *see* Bansa, Zeitsch. anorg. Chem. 1894, 6, 128. 143; Schwarz, *ibid.* 9, 249; Schulten, Bull. Soc. chim. [iii.] 2, 300; Ferrand, *ibid.* 1895, [iii.] 13, 115; Compt. rend. 1896, 122, 621, 886; Friedel, *ibid.* 1894, 119, 260).

Some natural zinc phosphates, viz. *hopeite* $Zn_3P_2O_8,4H_2O$; *parahopeite*, same formula; and *tarbuttite* $Zn_3P_2O_8Zn(OH)_2$ are described by Spencer (Min. Mag. 1908, 15, 1).

Zinc permanganate $Zn(MnO_4)_2,6H_2O$ may be prepared by adding a concentrated solution of zinc sulphate to a similar solution of barium permanganate so long as barium sulphate is precipitated. The solution is filtered, and the filtrate evaporated to crystallisation at a low temperature, or *in vacuô* over sulphuric acid, and the crystals finally dried at about 40°.

Zinc permanganate forms crystalline granules of a violet-brown colour, and is very soluble in water. In very dilute solutions it has been used successfully in the treatment of urethritis. It has no irritating action, but, like the potassium salt, it should never be compounded with alcohol, glycerol, sugar, or dry or fluid vegetable extracts as there may be danger of explosion owing to the readiness with which it is reduced and evolves oxygen (Merck, J. Soc. Chem. Ind. 1890. 409; Klobb, Bull. Soc. chim. [iii.] 9, 105).

Zinc orthosilicate Zn_2SiO_4 occurs native as *Willemite*. *Silicious calamine*, used to some extent as an ore of zinc, is a hydrated orthosilicate Zn_2SiO_4,H_2O. It is found in unsymmetrically-terminated rhombic prisms, and, like tourmalin, boracite, sugar, and other unsymmetrical crystals, it is pyro-electric—that is, on warming, one end becomes positively, the other negatively, electrified.

Amorphous zinc silicate is prepared by precipitating a solution of zinc sulphate with sodium silicate. When heated with boric acid for 10 days at a high temperature it forms a white crystalline powder of $ZnSiO_3$ insoluble in acids and isomorphous with the mineral *enstatite* (Traube, Ber. 1893, 26, 2735).

For some double zinc silicates, *see* Wyrouboff, Bull. Soc. Franc. Min. 1896, 19, 219; Wolff, Zeitsch. Kryst. Min. 1900, 33, 147; Duboin, Compt. rend. 1905, 141, 254.

Zinc sulphide *v. supra.*

Zinc chromate *v. Chromium.*

Zinc also forms *arsenates, thioarsenates*, and *arsenites* (Reichard, Ber. 1894, 21, 1019; *ibid.* 1898, 31, 2163; Lefèvre, Compt. rend. 1890, 110, 405; Preis, Annalen, 1890, 257, 178; Avery, J. Amer. Chem. Soc. 1906, 28, 1155); *antimonates* and *thioantimonates* (Senderens, Bull. Soc. chim. 1899, [iii.] 21, 47; Pouget, Ann. Chim. Phys. 1899, [vii.] 18, 508); *tellurates* (Gutbier, Zeitsch. anorg. Chem. 1902, 31, 340); *selenides* (Fonzes-Diacon, Compt. rend. 1900, 130, 832); *plumbates* (Hoehnel, Arch. Pharm. 1896, 234, 397); *ferrocyanides* (Stone and Ingen, J. Amer. Chem. Soc. 1897, 19, 542; Miller and Matthews, *ibid.* 547); and other compounds.

ORGANIC COMPOUNDS OF ZINC.

Zinc acetate $Zn(C_2H_3O_2)_2,2H_2O$ is prepared by neutralising acetic acid with zinc carbonate or oxide. It forms thin, soft, white, glistening, translucent plates, or monoclinic crystals of a pearly lustre soluble in water and in alcohol (Ley, Zeitsch. physikal. Chem. 1899, 30, 243). It closely resembles the sulphate in its action and uses.

Zinc oleate (*shoemaker's zinc oleate*) is prepared by dissolving 32 grms. of hard soap shavings in 480 c.c. of distilled water, heating, if necessary; 64 grms. of zinc sulphate are dissolved in 64 c.c. of boiling water and added to the former solution; after stirring, the oleate is separated, washed with hot water until free from sulphate, cooled, dried, and powdered (Naylor, Pharm. J. 1901, 66, 392). It is used in medicine as a mild astringent ointment and as an absorbent dusting powder to retain perspiration.

Zinc stearate is formed by the interaction of zinc acetate and sodium stearate. It is a fine white, tasteless powder, used for similar purposes as the oleate.

Zinc valerate $Zn(C_5H_9O_2)_2$ is prepared by mixing zinc sulphate with sodium valerate. It forms white, lustrous, pearly scales, or a white powder having the odour of valeric acid and a sweet, astringent metallic taste. It is also employed in medicine.

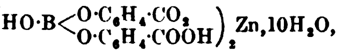
Zinc oxalate, propianate, tartrate, salicylate, and **lactate** have also been prepared. The last of these has been recommended for use in mordanting cotton and other vegetable fibres (Eng. Pat. 372, 1896; J. Soc. Chem. Ind. 1896, 804).

For the preparation of *zinc tannate, see* Villon, Bull, Soc. chim. 1890, [iii.] 3, 784.

Zinc antipyrine salicylate is formed when a dilute solution of sodium salicylate and antipyrine is mixed with a solution of zinc chloride or sulphate. It forms colourless needles, m.p. 75°–76° (decomp.), sparingly soluble in cold, and more so in warm, water, alcohol, and ether (Schuyten, Chem. Zentr. 1898, ii. 704).

Zinc boropicrate (*Chrysyl*) is obtained by the saturation of boropicric acid (prepared by boiling together 349 grms. picric acid, 62 grms. boric acid, and about 4 grms. of water) with 82 grms. of zinc oxide. It is a yellow powder used as a medicinal antiseptic (Monteil, J. Soc. Chem. Ind. 1908, 354).

Zinc boro-diorthohydroxybenzoate



$$\left(HO{\cdot}B{<}\begin{matrix}O{\cdot}C_6H_4{\cdot}CO_2\\O{\cdot}C_6H_4{\cdot}COOH\end{matrix}\right)_2Zn,10H_2O,$$

m.p. 100° (decomp.), is obtained by mixing 1 part boric acid with 1 of zinc carbonate, and 3 of salicylic acid, and adding the mixture in small portions to 10 times the weight of water at 65°. The mixture is agitated until no more carbon dioxide is evolved, when it is filtered and allowed to crystallise (Fr. Pat. 411614, 1910; J. Soc. Chem. Ind. 1910, 976).

Zinc compounds of 2-hydroxynaphthalenesulphonic acid-1-azo-β-naphthols have been prepared by treating 1-amino-2-naphthalsulphonic acids in concentrated aqueous solution, or in suspension, with alkali nitrite and an equivalent amount of zinc sulphate. The product so obtained is then made to react with a concentrated alkali solution of β-naphthol. The products dye wool in acid solution, bluish-red to violet shades, which turn bluish-black on subsequent treatment with a dichromate (U. S. Pat. 807422, 1905).

Basic zinc formaldehyde hydrosulphite is formed by adding 1 molecule of zinc to a mixture of 2 molecules of sulphurous acid and 2 of formaldehyde and then reducing the mixture by another molecule of zinc (U.S. Pats. 814032, 812124, 1906; J. Soc. Chem. Ind. 1906, 311, 217).

By the interaction of zinc-dust, sulphur dioxide, and aqueous formaldehyde, a difficultly soluble *zinc formaldehydesulphoxylate*, or a readily-soluble *zinc formaldehyde hydrosulphite* is formed, according to the conditions of the experiment (Eng. Pat. 81, 1906; J. Soc. Chem. Ind. 1906, 260; *see* also *ibid.* 1908, 1058; Becker, Ber. 1910, 43, 856; Fromm and Palma, *ibid.* 1906, 39, 3317; D. R. PP. 214041, 172217).

Zinc indigo white $C_{16}H_{10}O_2N_2Zn$ (?) is produced by the action of zinc chloride on calcium indigo white; of zinc oxide on indigo white in boiling naphthalene, and of zinc dust on indigotin in boiling naphthalene. It crystallises in lustrous leaflets (Binz, J. pr. Chem. 1901, [ii.] 63, 497).

Zinc gelatose is obtained by dissolving gelatose (formed by the action of superheated steam on gelatin) in dilute alcohol, adding a solution of a zinc salt and precipitating with alcohol. It is an amorphous powder, soluble in water, but insoluble in ether, benzene, and chloroform. It is said to be a valuable astringent without any irritating action on the mucous membrane (U.S. Pat. 698694, 1902).

Zinc chlorophyll is obtained by the action of zinc hydroxide and carbon dioxide on an alcoholic solution of chlorophyll. It closely resembles chlorophyll in properties. When treated with alkalis it yields a substance closely analogous with alkachlorophyl, but containing zinc instead of magnesium (Marchlewski, Biochem. Zeitsch. 1909, 16, 3).

Zinc *p*-**haemoglobin** $C_{758}H_{1139}Zn_2S_3FeO_{218}$ formed by shaking blood with zinc-dust or by the action of zinc salts on crystalline blood pigment, is a non-toxic compound, which has been recommended for use in the treatment of chlorosis (Grahe, Chem. Zentr. 1894, i. 636).

Zinc chloride forms stable double salts with diazo or tetrazo compounds of amino-azo or diamino-azo bodies which can be employed in dyeing (Eng. Pat. 1645; J. Soc. Chem. Ind. 1897, 40).

The diazo solution is prepared in aluminium or enamelled iron vessels, the requisite amount of zinc chloride is then added gradually with continual stirring. The double salt is formed as a voluminous precipitate, which, after settling, is filtered. When mixed with cold tragacanth thickening these double salts may be preserved unchanged for several days.

The goods prepared with sodium β-naphthol, to which sodium acetate is added, are printed with this paste, and then passed through a weak hydrochloric acid bath, washed, and soaped. The most satisfactory results have been obtained with α-naphthylamine hydrochloride, which yields a bright cardinal of a yellowish tone (Smirnoff and Rosenthal, Färber-Zeit. 7, 442).

Zinc chloride also forms double compounds, with fatty acids, with aliphatic compounds having a basic character, with aromatic bases containing one benzene nucleus, and with such compounds as piperidine, pyridine, and picoline (Lachowicz and Bandrowski, Monatsh. 1888, 9, 510; Bose, Amer. Chem. J. 1898, 20, 246; Bömer, Zeitsch. Nahr. Genussm. 1898, [viii.] 541).

The *zinc alkyl compounds* are formed, for the most part, by the action of the required alkyl iodide on zinc (Frankland and Duppa, Annalen, 1864, 130, 118; Gladstone and Tribe, Chem. Soc. Trans. 1879, 569; Fileti and Cantalupo, Gazz. chim. ital. 22, ii. 387; Ipatieff, J. pr. Chem. 1896, [ii.] 53, 257; Simonowitsch, Chem. Zentr. 1899, i. 1066; Worobéeff, *ibid.* 1067; Bohm, *ibid.* 1067; Ragosin, J. Russ. Phys. Chem. Soc. 1892, 24, 549; Lachman, Amer. Chem. J. 1900, 24, 31; J. Amer. Chem. Soc. 1901, 23, 897; Granichstädten and Werner, Monatsh. 1901, 32, 315; Haase, Ber. 1893, 26, 1052).

Zinc methyl is a colourless liquid, b.p. 46°, m.p. −40°, sp.gr. 1·386 at 10·5°, inflammable in air and decomposed by water.

Zinc ethyl is a colourless liquid, b.p. 118°, m.p. −28°, sp.gr. 1·182 at 18°; it has similar properties to the methyl compound.

The zinc alkyl compounds are employed in the synthesis of many organic compounds (Grigorovitch and Pawloff, J. Russ. Phys. Chem. Soc. 1891, 23, 159; Bewad, *ibid.* 1900, 32, 420; Tichwinsky, *ibid.* 1903, 35, 155; Gwosdoff, *ibid.* 339; Saytzeff, *ibid.* 1907, 39, 1232; Lachman, Amer. Chem. J. 1896, 18, 372; Bamberger and Tichwinsky, Ber. 1902, 35, 4179; Menschikoff, J. pr. Chem. [ii.] 36, 347; Bewad, *ibid.* 1907, [ii.] 76, 62; Saytzeff, *ibid.* 98; Blaise and Maire, Ann. Chim. Phys. 1908, [viii.] 15, 556; Compt. rend. 1907, 145, 73; *ibid.* 1909, 148, 489; Blaise, *ibid.* 1907, 145, 1285; Blaise and Herman, *ibid.* 1908, 146, 479; Delacre, Bull. Soc. chim. [ii.] 48, 784; Wagner, *ibid.* [ii.] 42, 330).

Zinc ethoxide $Zn(OEt)_2$ is formed by the action of zinc methyl on ethyl alcohol in an atmosphere of carbon dioxide, or, better, nitrogen or hydrogen. It is a white powder which cannot be distilled, is insoluble in ordinary solvents and readily absorbs moisture from the air. Zinc *iso*butyl oxide is similarly prepared by employing the corresponding alcohol (Tolkatscheff, J. Russ. Phys. Chem. Soc. 1901, 33, 469).

Other zinc organic compounds have been described by Moitessier (Bull. Soc. chim. 1899. iii. 21, 336); Werner (Zeitsch. anorg. Chem. 1899, 21, 201); Rosenheim and Meyer (*ibid.* 1906, 49, 13); Grossmann and Schück (*ibid.* 50, 1, 21); Ebler and Schott (J. pr. Chem. 1909, [ii.] 79, 72); also in D. R. P. 86148.

For methods of detecting and estimating zinc *v.* Analysis.

ZINC BLENDE *v.* Blende.

ZINC-DUST (VALUATION OF). Klemp has devised a process for the above purpose which depends on the power of zinc to reduce potassium iodate to potassium iodide in an alkaline solution. When the solution is afterwards acidified, iodine is liberated by the interaction of the iodic and hydriodic acids, and is distilled off from the mixture into potassium iodide solution, and titrated with thiosulphate. The details of the method are as follows:—

0·5–1 grm. of the well-mixed zinc-dust is weighed in a tube, and poured into a 200 c.c. stoppered flask, the tube being again weighed. For every 0·1 grm. of zinc present, 10 c.c. of a solution of alkali (containing 370 grms. of potassium hydroxide, or 300 grms. of sodium hydroxide per litre), and 3 c.c. of a solution of potassium iodate (containing 15·25 grms. of potassium iodate per 300 c.c.) are measured into a beaker, and then poured into the flask. Some glass beads are added, and the flask stoppered and shaken for 5 mins. in the cold, no advantage being gained by heating it. Its contents are then washed into a 250 or 500 c.c. flask, and made up to the mark with water. 100 c.c. are now pipetted into the retort of a Topf's apparatus (Zeitsch. anal. Chem. 26, 293), dilute sulphuric acid is added, and the apparatus filled with carbon dioxide. A solution of potassium iodide is placed in the receiver, and the retort heated, at first gently, and then more strongly till the contents are perfectly colourless. The stream of carbon dioxide is continued throughout the distillation, which generally occupies about 20 mins. The solution of iodine in potassium iodide is then transferred from the receiver into a flask, a standard solution of sodium thiosulphate added in slight excess, and the excess titrated back with weak standard iodine solution, starch being used as an indicator. After correcting for the excess, the quantity of zinc is calculated from the amount of thiosulphate used.

Klemp finds that the addition of powdered lead and iron to the zinc makes very little difference in the quantity of zinc found by this process, the results being a little lower in the presence of these metals.

The results by this method agree well with those obtained by Fresenius's method, but are generally higher than those obtained by Drewson's and lower than those obtained by Topf's method (G. Klemp, Zeitsch. anal. Chem. 29, 253–266; J. Soc. Chem. Ind. 9, 968). For a volumetric method, depending on the amount of hydrogen evolved by the action of an acid on zinc-dust, v. *ibid.* 5, 145, 1886.

ZINC FLOWERS. Zinc oxide produced by combustion; *v.* Zinc.

ZINC GREEN, *Cobalt green,* or *Rinmann's green*; *v.* Cobalt; also Pigments. This term is also applied to a mixture of zinc yellow and Prussian blue.

ZINCITE. Native zinc oxide ZnO, crystallising in the hexagonal system. The crystals, which are of rare occurrence, possess the same degree of symmetry (hemimorphic-hemihedral) and very nearly the same angles as those of wurtzite (ZnS) (*q.v.*). The mineral is usually found as lamellar cleavage masses (there being a perfect basal cleavage), which are opaque to translucent and deep-red, rarely orange-yellow, in colour. The streak is orange-yellow; sp.gr. 5·6. Manganous oxide (3–6 p.c.) replaces part of the zinc, and there is often a little ferric oxide present. Zincite is known only from the zinc mines at Franklin Furnace and Sterling Hill in Sussex Co., New Jersey, but it occurs there in considerable abundance, and is mined, together with franklinite and willemite, as an ore of zinc. Fragments of the mineral have also been used in the wave detectors of wireless telegraphy installations. White or yellowish crystals of hexagonal zinc oxide have often been observed in zinc furnaces, and sometimes in iron furnaces. L. J. S.

ZINCOPYRIN. Trade name for phenyldimethyl-pyrazolone zinc chloride

$$(C_{11}H_{12}N_2O)_2\cdot ZnCl_2$$

first obtained by Schuyten. Shining scales, m.p. 156°. Readily soluble in water, alcohol, and chloroform. Used in the treatment of inoperable carcinoma of the uterus.

ZINC SPAR. Syn. with calamine; *v.* Zinc.

ZINC VITRIOL. *Zinc sulphate v.* Zinc.

ZINC WHITE *v.* Zinc.

ZINC YELLOW, or *Buttercup yellow* and *Zinc chromate, v.* Chromium.

ZINKENITE or **ZINCKENITE.** *Lead sulphantimonite v.* Antimony.

ZINNWALDITE *v.* Mica.

ZINOL *v.* Synthetic drugs.

ZIRCON. Native zirconium silicate $ZrSiO_4$, crystallising in the tetragonal system and homœomorphous with cassiterite and rutile. A little ferric oxide (0–3 p.c.) and sometimes thoria are present. The mineral varies considerably in its characters and appearance; and further, several altered and hydrated forms are distinguished by special names (*malacon, cyrtolite, oerstedite,* &c.). The transparent gem-varieties show a wide range in colour; brownish-yellow and red specimens are known as *hyacinth* (or jacinth), and yellowish and green as *jargon* (or jargoon). The colour can usually be changed by heat, and some brownish-yellow stones are completely decolorised. With their brilliant adamantine lustre, these artificially decolorised stones ('Matura diamonds,' from Matura in Ceylon) may be mistaken for diamond. The hardness is 7½. The mineral is remarkable in showing a wide range in sp.gr. (4·0–4·7), and in optical characters, and these sometimes undergo a marked change when the crystals are heated to redness. These differences and changes suggest the existence of three modifications of zircon, which may occur as intergrowths in the zoned crystals (L. J. Spencer, Min. Mag. 1904, 14, 48).

Zircon occurs as a primary constituent of many igneous rocks, but, as a rule, only as minute crystals. Being heavy, hard, and resistant to weathering agencies, it collects in the beds of streams. Most of the gem material is obtained from gem-gravels in Ceylon and Australia. Rough and opaque zircon has been mined in considerable quantity in Henderson and Buncombe counties, North Carolina, and in Brazil. It is employed as a source of zirconia, used in incandescent gas-lighting and in electric arc-lamps. L. J. S.

ZIRCONIUM. Sym. Zr. At.wt. 90·6. Zirconia, the oxide of this metal, was identified in 1879 by Klaproth, who obtained it from the zircon of Ceylon, and this observation was confirmed by Guyton and Vauquelin. Zirconium is sometimes included in the group of rare earth metals, although in its quadrivalency, and in the amphoteric nature of its oxide, it is distinctly unlike the typical members of this series.

Occurrence.—As the main constituent in zircon and malacon, which are found as accessory minerals in many metamorphic and igneous rocks (granites, syenites, elæolite-syenites, basalts, amphibolites), and in baddeleyite (brazilite). Large deposits of zirconia earth have been found in São Paulo, Brazil (*cf.* Fletcher, Min. Mag. and J. Min. Soc. 1893, 10, 148; Hussak and Reitinger, Zeitsch. Krist. 1903, 37, 567; Wedekind, Zeitsch. angew. Chem. 1908, 21, 2270; Ber. 1910, 43, 290). Brazilian zirconia deposits are feebly radioactive, and on ignition evolve a gas containing argon and helium (Zeitsch. Elektrochem. 1908, 14, 585; Ann. Chim. Phys. 1898, [vii.] 13, 433; Chem. Soc. Trans. 1906, 89, 1568; 1908, 93, 350). The following minerals contain a high percentage of zirconium: *zirkelite* (zirconium titanate with thoria and rare earths), *eudialite* (*eukolite*), *elpidite, katapleite* (zirconium double silicates of sodium and calcium), *polymignite* (Norway, a complex zircono-silicate, with titanium and tantalum oxides, columbium oxide, thoria, and the rare earths). Zirconium is a minor constituent of all rare-earth minerals (*v.* Cerite earths), and is found also in *pitchblende, columbite,* and *tantalite.*

Separation and purification of zirconia.

1. *Fusion with sodium carbonate or hydroxide.* The native silicate (zircon) disintegrated by heating and dropping into water, is extracted with hydrochloric acid to remove metallic impurities (iron, &c.) and fused with sodium carbonate or hydroxide (4 parts) containing 10 p.c. of sodium fluoride. When extracted with water the fused mass leaves an insoluble crystalline precipitate of sodium zirconate, which is dissolved in hydrochloric or sulphuric acid, and the zirconium hydroxide precipitated by ammonia (Monatsh. 1885, 6, 531; Chem. Soc. Trans. 1889, 58, 705; Amer. Chem. J. 1892, 5, 551).

2. *Decomposition with hydrofluoric or sulphuric acid, or their acid salts.* Zircon is exposed to the vapour of hydrogen fluoride or heated with potassium hydrogen fluoride, and,

in the latter case, the product, when boiled with hydrofluoric acid, leaves a deposit of potassium silicofluoride, whilst the more soluble potassium zirconofluoride crystallises out on concentrating the solution (J. 1859, 677; Ann. Chim. Phys. 1860, [iii.] 60, 257). Zircon can also be decomposed with hot concentrated sulphuric acid, or with fused potassium hydrogen sulphate (Ber. 1870, 3, 58; Annalen, 1876, 181, 232).

3. *Reduction with carbon or calcium carbide.* Crude zirconium carbide obtained by heating an intimate mixture of zircon and carbon in the electric furnace is heated in chlorine, and the resulting chloride dissolved in concentrated hydrochloric acid; the crystalline oxychloride, which separates from this solution, is decomposed by ammonia. A mixture of zircon, calcium oxide, and carbon is heated in the electric furnace (1030 ampères, 50 volts for 7 mins.); the product, when extracted with water and dilute hydrochloric acid, is decomposed by chlorine at 300°, yielding zirconium chloride (Compt. rend. 1893, 116, 1428; 1896, 122, 651; Zeitsch. anorg. Chem. 1902, 33, 81; Ber. 1902, 35, 3929; Chem. Zeit. 1907, 31, 654).

4. *Other methods of purification.* Zirconia is freed from silica by heating with potassium hydrogen fluoride when the latter oxide is eliminated as volatile silicon fluoride. Crude zirconia is rendered soluble by heating with strong sulphuric acid or by fusion with sodium hydrogen sulphate. Treatment of the product with warm water leads to the separation of crystalline basic sulphate (Ber. 1904, 37, 2024; *cf.* Zeitsch. anorg. Chem. 1905, 45, 155). Zirconia is freed from iron by crystallising the oxychloride from strong hydrochloric acid (Chem. Soc. Trans. 1889, 58, 705; Amer. Chem. J. 1891, 5, 551; J. Amer. Chem. Soc. 1894, 16, 469). Ferruginous zirconium hydroxide, when dissolved in hydrochloric acid and boiled with sodium thiosulphate, gives the pure hydroxide mixed with sulphur. The addition of ammonia and ammonium sulphide to an iron and zirconium solution precipitates zirconium hydroxide, and ferrous sulphide, the latter being dissolved out with sulphurous acid. In the presence of tartaric acid the foregoing solution yields ferrous sulphide alone on adding ammonium sulphide; the concentrated filtrate, when mixed with excess of hydrogen peroxide, furnishes pure hydrated zirconium peroxide (Zeitsch. anorg. Chem. 1902, 33, 81). Brazilian zirconia earth (74–94 p.c. ZrO_2) is dissolved in mineral acid, and the iron and titanium removed from the dilute solution with ammonia and ammonium carbonate, the liquid being warmed until it gives no coloration with sulphuric acid and hydrogen peroxide. The acidified filtrate is boiled to expel carbon dioxide and the zirconium hydroxide precipitated with ammonia. The mineral may also be heated with magnesium in an atmosphere of hydrogen; the product extracted successively with ammonium chloride, hydrochloric acid, and potassium hydroxide to remove magnesium, iron, and silicon; the residue is heated in hydrogen, and then in chlorine or bromine, when zirconium chloride or bromide sublimes (Wedekind, Ber. 1910, 43, 290).

Zirconium is isolated only with difficulty owing to the readiness with which it combines with oxygen, nitrogen, carbon, silicon, &c. When reduced with carbon in the electric furnace zirconia yields zirconium containing either oxide or carbide, depending on the proportion of the reagents (Troost, Compt. rend. 1893, 116, 1227; Moissan, *ibid.* 1222; Greenwood, Chem. Soc. Trans. 1908, 93, 1483). Boron or silicon reacts with zirconia in the electric furnace, but the product is contaminated with boride Zr_3B_4 or silicide. Amorphous zirconium (95–96 p.c. Zr) is obtained by heating potassium zirconofluoride with sodium under fused potassium chloride in closed iron vessels, the product being extracted with alcohol and then with hydrochloric acid. By reducing the double fluoride with aluminium at the temperature of melting iron impure metallic zirconium (98 p.c.) is produced, but in the electric furnace an alloy of this element and aluminium is formed. Reduction of the double fluoride with magnesium in the electric furnace gives crystalline zirconium (94 p.c.), but sometimes contaminated with nitride. The product, containing 97–98 p.c. of zirconium, is pressed into rods, and then used as the terminals of an electric arc operating in hydrogen under diminished pressure; fusion takes place, and 99·8 p.c. zirconium is obtained. This resembles white cast iron, and has a hardness 7–8, sp.gr. 6·40 at 18°, sp.ht. 0·0804, and heat of combustion (1 grm.)=1958·7 cals. The amorphous variety, which is a black powder, and a bad conductor of electricity, is readily oxidisable, whereas the crystalline modification yields zirconia only at white heat. An intermediate oxide Zr_2O_3 has been recognised, which is slowly oxidised to the dioxide. Zirconium is attacked by hydrogen fluoride or by *aqua regia*, and at red heat by hydrogen chloride or chlorine, but is not appreciably affected by sulphuric, hydrochloric, or nitric acid; it is oxidised by fused potassium hydroxide or nitrate (Zeitsch. anorg. Chem. 1905, 45, 385; 1910, 65, 248; Zeitsch. Elektrochem. 1904, 10, 331; Annalen, 1910, 371, 367). Zirconium has also been prepared by reducing zirconia with metallic calcium (Eng. Pat. 23215, 1909).

Zirconia (*Zirconium dioxide*) ZrO_2 occurs native as *baddeleyite* in monoclinic forms, not isomorphous with cassiterite or rutile. When crystallised from borax a quadratic form of zirconia is produced isomorphous with rutile. Ignition of zirconium hydroxide, sulphate, oxalate, or nitrate yields the dioxide as a hard white powder. The density varies with the mode of preparation, unfused specimens having sp.gr. 5·4824 at 18·5°, whilst fused rods vary from 5·48–5·75. Zirconia is extremely infusible and non-volatile, although it has been melted and vaporised in the electric furnace (360 ampères, 70 volts). The vapour condenses to a fine powder which scratches glass. The sp.ht. of zirconia is 0·1076; it is a bad conductor of heat, and has a linear coefficient of expansion=0·00000084, near to that of fused quartz (Nilson and Petterson, Compt. rend. 1880, 91, 232; Moissan, *ibid.* 1893, 116, 1222; Lehman, Dissert. Techn. Hochsch. München. 1908; Zeitsch. anorg. Chem. 1909, 65, 178).

The solubility of zirconia in mineral acids depends on the temperature of ignition; after slight ignition it dissolves readily, but after strong ignition it becomes practically insoluble.

although it is attacked by hydrofluoric and concentrated sulphuric acids.

When heated in the oxy- coal gas flame zirconia becomes brilliantly incandescent, so that it may replace for certain special purposes the lime of the Drummond light, and it has been thus employed by Linnemann and others in spectroscopy and microphotography. It has received an important technical application in the Nernst lamp in which the incandescent body is composed chiefly of zirconia (85 p.c.), together with oxides (15 p.c.) of the yttrium series. This material conducts only at high temperatures, so that it requires to be first heated before the electric current can be transmitted.

Strongly ignited zirconia is very stable towards acids and alkalis, and as it is not fractured by sudden changes of temperature, it may be employed for crucibles in which platinum and quartz can be melted. Refractory vessels have also been made from zirconia mixed with 10 p.c. of magnesia or clay, phosphoric acid being employed as a binding material (Zeitsch. anorg. Chem. 1909, 65, 178).

Zirconia crucibles are moulded from the plastic mass made by kneading together gelatinous zirconium hydroxide and artificial or purified native zirconia, a little starch being added to keep the mass firm while drying. After 2 days the crucibles are gently heated at 50°–100°, and the temperature then raised gradually to 2000°–2300°. These crucibles are not affected by fused alkalis or alkaline bisulphates (Bayer, Zeitsch. angew. Chem. 1910, 23, 488).

Zirconium hydroxide behaves as an amphoteric hydroxide, its compounds with the alkalis undergoing considerable hydrolysis in aqueous solution. The zirconates are produced either by adding zirconium salts (*e.g.* nitrate) to concentrated alkali solution, or by fusing zirconia with the alkaline hydroxides or oxides. The substances obtained by the wet process are probably adsorption products rather than definite chemical compounds, for prolonged washing gradually removes the alkali from the colloidal mass. The fusion process leads to *meta*zirconates $CaZrO_3$, Na_2ZrO_3, and Li_2ZrO_3, but even these products vary somewhat in composition. Other types, such as $Li_2Zr_2O_5$ have been described. When zircon (zirconium silicate) is fused with alkalis the crystalline silicozirconates are obtained, *e.g.* $K_2O(SiO_2,ZrO_2)$ and $CaO(SiO_2,ZrO_2)$, the latter being isomorphous with titanite (Ouvrard, Compt. rend. 1891, 112, 1444; 113, 80).

Colloidal insoluble zirconium hydroxide (hydrogel) is produced by boiling solutions of zirconium oxychloride (Ruer, Zeitsch. anorg. Chem. 1905, 43, 282; van Bemmelen, *ibid.* 1906, 49, 125). The hydrosol modification is prepared by adding ammonia to aqueous zirconium nitrate or by dissolving freshly-precipitated zirconium hydroxide in this solution (Müller, *ibid.* 1907, 52, 316).

Zirconium peroxide is produced as a gelatinous precipitate by adding ammonia to aqueous zirconium sulphate containing hydrogen peroxide; or by the electrolysis of an alkaline sodium chloride solution in which zirconium hydroxide is suspended. The product is probably $Zr(OH)_3{\cdot}O_2H$, a hydrated form of ZrO_3 (Pissarjewski, Zeitsch. anorg. Chem. 1899, 25, 378; 1900, 31, 359; *v.* Bailey, Chem. Soc. Trans. 1886, 49, 149, 481; 1889, 58, 705).

The alkali *perzirconates* $Na_4Zr_2O_{11},9H_2O$ and $K_4Zr_2O_{11},9H_2O$ are precipitated by alcohol, from cold aqueous alkaline solutions of the hydrated peroxide and hydrogen peroxide.

Zirconium hydride ZrH_2, black powder, produced from metallic zirconium and hydrogen at red heat, burns in oxygen under ordinary pressure to the sesquioxide Zr_2O_3, and in the compressed gas to zirconia.

Zirconium fluoride ZrF_4, anhydrous, sp.gr. 4·4333 at 16°, sparingly soluble in cold water, hydrolysed on warming, prepared by heating zirconia with ammonium hydrogen fluoride. The hydrate $ZrF_4,3H_2O$, triclinic crystals, obtained by dissolving zirconia in hydrofluoric acid.

Zirconofluorides. These double fluorides are of especial interest because of their use in the purification of zirconium compounds and in the isolation of the element itself, and also because they illustrate the family relationship subsisting between zirconium and the other elements (silicon, titanium, and tin) of the fourth periodic group. Moreover, the existence of these well-defined crystallisable double salts distinguishes zirconium from the rare earth metals. They are produced by dissolving zirconium fluoride or oxide together with a metallic oxide or carbonate in aqueous hydrogen fluoride. The zirconofluorides corresponding with the general formula $R^I_2ZrF_6$ are the most stable, although other forms exist (Marignac, Compt. rend. 1860, 50, 952; Wells and Foote, Zeitsch. anorg. Chem. 1896, 10, 434; Amer. J. Sci. 1897, [iv.] 3, 466).

Potassium zirconofluoride K_2ZrF_6, rhombic prisms, is the most important compound of this series; 100 parts of water dissolve 0·78 part of the salt at 2°, and 25·0 parts at 100°.

Zirconium chloride $ZrCl_4$ can only be obtained pure by dry processes owing to its great tendency to undergo partial hydrolysis. The following methods have been employed.

(i.) The action of chlorine and sulphur chloride on heated zircon (Matignon and Bourrion, Compt. rend. 1904, 138, 631). Formerly carbon was used as the reducing agent instead of sulphur chloride. The chlorides of silicon and titanium are also produced in this process, but are readily separated owing to their greater volatility.

(ii.) The interaction at 300° of zirconium carbide, and chlorine (Wedekind, Zeitsch. anorg. Chem. 1902, 33, 81).

(iii.) Sublimation in chlorine of the product obtained by heating zirconia and phosphorus pentachloride in sealed tubes at 190° (Smith and Harris, J. Amer. Chem. Soc. 1895, 17, 448; *v.* Venable, *ibid.* 1894, 16, 469; Annalen, 1887, 239, 253; Compt. rend. 1865, 61, 109; 1872, 75, 1819; 1887, 104, 113; Ber. 1887, 20, 683).

The anhydrous chloride is a white crystalline sublimate fuming in moist air, reacting energetically with water, and combining with 1–8 molecules of dry ammonia (J. Amer. Chem. Soc. 1898, 20, 815, 839, 843; Ber. 1905, 38, 2611). It forms additive compounds with phosphorus pentachloride and sulphur tetrachloride, and forms double chlorides $B_2H_2ZrCl_6$ with alcoholi pyridine and quinoline hydrochlorides (Ber. 1905, 38, 812).

Zirconium oxychloride $ZrOCl_2,8H_2O$, colourless tetragonal prisms, the most characteristic product of hydrolysis of the preceding compound, is somewhat sparingly soluble in concentrated hydrochloric acid, and is on this account utilised in the separation of zirconium. The addition of ether to an alcoholic solution of this oxy-salt produces a precipitation of *metazirconium chloride* $Zr_2O_3Cl_2$, corresponding with metastannic chloride. This product, which is practically insoluble in strong hydrochloric or nitric acid, dissolves in water to an opalescent colloidal solution, and this liquid on dialysis furnishes *metazirconic acid* (J. pr. Chem. 1875, [ii.] 2, 219; Ber. 1907, 40, 803; Zeitsch. anorg. Chem. 1904, 42, 87; 1905, 43, 282; 46, 456).

Zirconium bromide $ZrBr_4$, crystalline white powder, and **zirconium iodide** ZrI_4, yellowish-brown powder, are prepared by passing over heated zirconium or its carbide a stream of bromine vapour or hydrogen iodide respectively (Ber. 1904, 37, 1135; 1905, 38, 2611). The corresponding oxy-salts $ZrOBr_2,8H_2O$ and $ZrOI_2,8H_2O$ are produced by hydrolysing the foregoing bromides.

Zirconium carbide ZrC, hard metallic mass, scratching quartz but not ruby, is obtained by heating an intimate mixture of zirconia and carbon in the electric furnace (Moissan and Lengfeld, Compt. rend. 1896, 122, 651). A mixture of calcium carbonate, carbon, and zircon gives a similar result after extracting the fused mass with water and dilute hydrochloric acid. The carbide is also produced by heating native zirconia with carbon, using a current of 600 ampères (Wedekind, Ber. 1902, 35, 3929; Chem. Zeit. 1907, 31, 654). The carbide is an excellent conductor of electricity, and a mixture of 90 parts with 10 parts of ruthenium made into filaments has been suggested for use in incandescent lamps. When heated in nitrogen the carbide furnishes *zirconium nitride* Zr_2N_3 (*v.* Zeitsch. anorg. Chem. 1905, 45, 385).

Zirconium silicide $ZrSi_2$, iron-grey rhombic crystals, sp.gr. 4·88 at 22°, is prepared by the aluminothermic process (200 parts aluminium, 250 parts sulphur, 180 parts sand, and 40 parts potassium zirconofluoride covered with a thin layer of magnesium as priming). It is not attacked by acids except hydrofluoric acid, and is only decomposed by caustic potash at moderately high temperatures (Compt. rend. 1906, 143, 224; *v.* Ber. 1902, 35, 3929). A colloidal variety of zirconium silicide has been observed (Zeitsch. Chem. Ind. Kolloide, 1910, 7, 249).

Zirconium sulphates (1) '*neutral*' *sulphate* $Zr(SO_4)_2.4H_2O$ or *zirconylsulphuric acid*

$$ZrO(SO_4)_2H_2,3H_2O,$$

rhombic crystals from sulphuric acid solution, differs considerably in its properties from the oxychloride. The zirconium present is not precipitated as oxalate by oxalic acid or its soluble salts, and the precipitation which occurs with the aqueous chloride is prevented by the addition to this solution of sulphuric acid or an alkali sulphate. In hydrochloric acid solutions of the chloride the zirconium ion passes to the cathode on electrolysis, but in solutions of the sulphate the zirconium passes to the anode in the complex anion $(ZrOSO_4,SO_4)^{II}$ (*v.* Hauser, Zeitsch. anorg. Chem. 1905, 45, 185; 1907, 53, 74; 54, 196; J. pr. Chem. 1907, [ii.] 76, 363; Ruer, Zeitsch. anorg. Chem. 1904, 42, 87; 1905, 46, 449).

(2) *Basic sulphates* (i.) 4:3-*Basic sulphate* $4ZrO_2,3SO_3,14H_2O$, microscopic birefringent needles, separates at 39·5° from a solution of 10·2 molecules of $Zr(SO_4)_2$ in 1000 molecules of water. When dried at 300° the anhydrous compound $4ZrO_2,3SO_3$ is obtained (Ber. 1904, 37, 2024; Zeitsch. anorg. Chem. 1910, 67, 369).

(ii.) 2:3-*Basic sulphate* $2ZrO_2,3SO_3,5H_2O$ is obtained in a crystalline form by boiling concentrated solutions of zirconium sulphate; in cold water it gradually changes into the preceding basic salt.

(3) *Acid sulphate* $Zr(SO_4)_2,H_2SO_4,3H_2O$, monoclinic prisms or needles, is a very hygroscopic salt produced by adding strong sulphuric acid to an aqueous solution of zirconylsulphuric acid (Zeitsch. anorg. Chem. 1907, 54, 196).

(4) *Complex sulphates.* These are of two types $Zr_2O_3(SO_4R')_2,xH_2O$ and $Zr(SO_4R')_4,xH_2O$, where R is an alkali metal; the former are produced by adding an alkali sulphate to a solution of zirconium oxide in aqueous alkali disulphate and the latter by dissolving zirconium hydroxide in a boiling saturated solution of alkali disulphate (Ber. 1907, 40, 803, 810).

Zirconium nitrate $Zr(NO_3)_4,5H_2O$, colourless hygroscopic crystals, which may also be regarded as *zirconylnitric acid* $ZrO(NO_3)_4H_2,4H_2O$. Aqueous solutions of this compound yield on evaporation *basic nitrates* $ZrO(NO_3)_2,2H_2O$ and $Zr_2O_3(NO_3)_2,5H_2O$.

Zirconium oxalate is a basic salt, *zirconyl oxalate* $ZrO(C_2O_4),H_2O$ or $4H_2O$, white powder, hydrolysed by water. By saturating aqueous oxalic acid with zirconium hydroxide an *acid oxalate* $Zr(OH)(C_2O_4H)_3,7H_2O$ is obtained in large prisms. Double oxalates are produced by dissolving zirconium hydroxide in solutions of the alkali hydrogen oxalates (Mandl, Zeitsch. anorg. Chem. 1903, 37, 252; *v.* Venable and Baskerville, J. Amer. Chem. Soc. 1897, 19, 12).

Zirconium acetylacetonate

$$Zr[CH(CO{\cdot}CH_3)_2]_4,10H_2O$$

crystallises from an aqueous solution of zirconium nitrate and acetylacetone to which sodium carbonate is cautiously added; it is dehydrated by repeated crystallisation from absolute alcohol when it separates in needles. G. T. M.

ZYMASE *v.* FERMENTATION.

ZYMIN *v.* SYNTHETIC DRUGS.

ZYMURGY. A term used to denote that section of applied chemistry which treats of the scientific principles of those arts in which fermentation is employed—*e.g.* preparation of yeast, vinegar, wine, beer, alcohol.

THE END

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